PRODUCTION OF SUSTAINABLE CONCRETE USING INDIGENOUS SAUDI NATURAL POZZOLAN

BY

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TO

MY LOVING PARENTS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

THESIS ABSTRACT (ENGLISH)

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Saudi Arabia; along with the other Arabian Gulf countries, have been dominated by harsh environmental and aggressive exposure conditions. These conditions adversely affect the service life of concrete structures in this region. Now, it is well established that concrete structures for the local conditions need to be designed for durability rather than for strength and workability alone. Several methodologies have been suggested for this purpose, one of which is the incorporation of supplementary cementing materials.

Silica fume and fly ash are the most popular supplementary cementing materials used in the Kingdom. However, both fly ash and silica fume are not available locally. On the other hand, large reserves of natural pozzolan have been discovered in the western region of Saudi Arabia, but these types of pozzolan have low pozzolanic activity.

The objective of this research was to develop sustainable concrete utilizing the locally available natural pozzolan and to study the activation techniques (i.e. mechanical, chemical and physical) to increase its pozzolanic activity. The mechanical properties and durability characteristics of the developed natural pozzolan concrete were evaluated and compared with that of OPC concrete. Results of this investigation indicated that there is a great potential for incorporating indigenous natural pozzolan in order to upgrade the performance of concrete, particularly the durability characteristics. Therefore, the usage of locally available natural pozzolan, as a partial replacement of cement, is recommended in order to improve the durability of concrete and to decrease the greenhouse gas emission.

ملخص الرسالة (عربي)

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تتعرّض المملكة العربية السعودية مع غيرها من دول الخليج العربي الى ظروف بيئية قاسية تؤثر سلباًعلى العُمر الأفتراضي والحياة العملية للمنشآت الخرسانية في هذه المنطقة. وأصبح واضحاً الآن أن المنشآت الخرسانية في البيئات المحلية تحتاج لتكون مصممة لتحسين الديمومة وليس لزيادة القوة والمرونة فقط. وقد تمّ اقتراح عدة منهجيات لهذا الغرض، ومنها استخدام المواد الأسمنتية التكميلية أو المضافة.

وللعلم، فأن غبار السيليكا والرماد المتطاير هما الأكثر استخداماً من هذه المواد التكميلية المستخدمة في المملكة، وهما غير متوفرتان محلياً. ومن ناحية أخرى، تم اكتشاف احتياطيات كبيرة من البوزولان الطبيعي في المنطقة الغربية من المملكة العربية السعودية، ولكن هذه الأنواع من البوزولان لديها انخفاض في النشاط البوزولاني، مما لايؤهلها للأستخدام المباشر في الخرسانة.

كان الهدف الأساسي من هذا البحث هو تطوير خرسانة مستدامة باستخدام أنواع مختلفة من البوزولان الطبيعي المتاح محلياً ودراسة تقنيات التنشيط (الميكانيكية والكيميائية والفيزيائية) لزيادة نشاطها البوزولاني. وتمّ تقييم الخواص الميكانيكية وخصائص الديمومة لخرسانة البوزولان الطبيعي ومقارنتها مع تلك المصنوعة من الخرسانة الأعتيادية (OPC). وأشارت نتائج هذا البحث أن هناك إمكانات كبيرة لاستخدام البوزولان الطبيعي المحلي من أجل رفع مستوى الأداء من الخرسانة، ولا سيما خصائص الديمومة. ولذلك، يُستحسن استخدام البوزولان الطبيعي المتاح محلياً، كبديل جزئي للأسمنت، من أجل تحسين ديمومة الخرسانة وتقليل انبعاث الغازات المسببة للاحتباس الحراري.

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CHAPTER 1

INTRODUCTION

1.1 Utilization of Saudi Natural Pozzolan in Concrete

Structural concrete elements can be cast in factory as well as on site; this unique property of concrete makes it to be the most extensively used building material in the world. There are two main components of concrete; aggregate and binder. The most common choice for binder is cement, which in the presence of moisture, hydrates to develop the gluing properties which then binds the aggregates together. Upon hardening, this duo produces an artificial stone-like material that is called concrete.

Cement, in the form we know it today, was first produced in 1840s under the name of Portland cement [1,2] but it was not for the first time that binder was used in building structures. Romans were using a mixture of lime and volcanic ash called Pozzolana to make a mortar about 2000 years ago [1,2]. Egyptians were using lime mortar for laying stone blocks nearly 5000 years ago [1]. Also, cement production is still evolving and since 1840s there are different types of cements being manufactured other than Portland cement.

After the industrial revolution across the world steamed with coal and other fossil fuels, just recently we are getting more and more concerned about our living environment as individuals and earth's atmosphere as one global human community. This concern did

not leave aside evaluation of the mechanism of cement production and its impact on our environment. In the last 25 years, a lot of studies have been conducted and now it's a well established fact that the cement production industry is a major contributor in emission of carbon dioxide into the atmosphere. With the cement production reaching to 2.8 billion tons per annum in the year 2010 [2], cement industry is responsible for about 7% of globally emitted carbon dioxide in to the earth's atmosphere annually by all human activities compared to only 5% by the year 1990 [3].

Carbon dioxide is the most important and effective among all the green house gases [3]. These green house gases when present in earth's atmosphere do not allow sun's radiation and other sources of heat energy to leave earth's atmosphere causing increase in the mean temperature of earth (global warming). Other green house gasses include methane, nitrous oxide and chlorofluorocarbons (CFCs).

For every ton of cement produced about 900 kg carbon dioxide is being emitted into earth's atmosphere [1,3], of this amount about 50% comes from burning of fuel to achieve the high temperature required to produce cement [1,3] and the remaining 50% from chemical processes involving the decomposition of calcium carbonate into lime and carbon dioxide [1]. Over the years and with emergence of more economical, more abundantly available and more environment friendly fuels we have moved from fossil fuel to coal to pet coke to natural gas and now to alternate fuels but still we lack somewhere. Now, after so much time and energy consumed in making fuel more efficient, down the line we have start looking into reduce the consumption of cement itself [4]. Studies show that during the production of cement, 20-30% clinkers may be

replaced by natural pozzolan, fly, ash or slag [1], which helps in cutting down the production of carbon dioxide by 20% [2].

Further, Saudi Arabia and the other Arabian Gulf countries are exposed to the toughest climatic and geomorphic conditions in the world with fluctuating temperatures rising to 50°C in summer and dropping to as low as 2°C in winters, with sabkha soils containing high concentrations of salts that can come in contact with footings and foundations. Some regions do not receive any rain in years and are thus dry and are dominated by gusty sand storms having eroding properties, others have humid summers with humidity reaching up to 80% at night times exposing structures to wet and dry cycles. Such climate has its own adverse effects and concrete paying the toll and deteriorates at a much higher pace than other regions of the world.

Adding inert materials in concrete which can only act as fillers or use of pozzolanic materials as a partial replacement of cement in concrete have proven to enhance durability properties of concrete [5-13], also it helps in reducing the consumption of cement.

These supplementary cementing materials when introduced in a concrete mix react with calcium hydroxide $Ca(OH_2)$ produced during the hydration of cement to form calcium silicate hydrate (C-S-H). This reaction is called the pozzolanic reaction and such materials are called pozzolanic materials. Due to this additional C-S-H gel, we get dense concrete micro-structure.

In fact, blended cements incorporating pozzolanic materials have recently been specified in the Saudi Building Code for extreme exposure conditions [10]. Though supplementary cementing materials, such as fly ash, blast furnace slag and silica fume, have been extensively used by the construction industry, these materials are not produced in the Arabian Gulf countries and they are imported from other countries. Further, the cost of these materials has increased every year due to the increasing cost of transportation and higher demand. Additionally, shortage of these materials in the Saudi market has created several problems to the construction industry.

It was reported that the volcanic mountains located around the vicinity of Al-Madinah Al-Munawwarah, western Saudi Arabia, possess some pozzolanic properties. Since the cost of this natural pozzolan is less than that of the imported pozzolans, there is an exigent need to conduct a research on this "national" material. Initial studies conducted at KFUPM showed that this material barely meets the requirements of ASTM C618 to be classified as a pozzolanic material. This pozzolan may be used as a filler material but to upgrade its performance to qualify it for use as an active pozzolan, more in-depth studies have to be carried out.

1.2 Significance of this Research

The development of an alternative cementing material, utilizing the local resources, would be highly beneficial to the Kingdom. It would result in a significant saving in the cost of concrete, compared to that prepared utilizing imported supplementary cementing materials, such as silica fume and fly ash. The use of local pozzolanic material would

also eliminate the dependence on an external source. Another aspect of the development of an alternate blended material using local resources is that it will result in a reduction in the consumption of cement. Since the production of cement is a highly energy intensive process and releases significant quantity of green-house gases, a reduction in its usage will lead to a decrease in the carbon footprint of the kingdom.

1.3 Objective

The overall objective of this study was to produce sustainable concrete utilizing the indigenous natural pozzolan and, if required, to improve its quality for use in concrete. The specific objectives were as follows:

1. To characterize the properties of indigenous natural pozzolan;
2. To enhance the reactivity of the local natural pozzolan either mechanically by increasing its surface area, or physically by adding a more reactive "super-pozzolanic" material (i.e. silica fume) at small dosages, or chemically by adding an alkaline material (i.e. hydrated lime or soda);
3. To investigate the mechanical properties of mortar/concrete mixtures prepared with the modified pozzolan-blended cements; and
4. To assess the durability of the developed pozzolan-blended cement concretes.

CHAPTER 2

LITERATURE REVIEW

2.1 Pozzolanic Materials

Blended cement is a mixture of a Portland cement and a pozzolan or an industrial byproduct. According to ASTM C 618, pozzolans are defined as siliceous or siliceous and aluminous materials that possess no cementitious properties by themselves but, in the presence of moisture, they react, at normal temperature, with lime that is generated during hydration of cement to form secondary calcium silicate hydrate [7].

The pozzolanic materials include a variety of natural and artificial products. ASTM C 618 Type N defines the natural pozzolan (NP) as volcanic ash and diatomaceous earth. These materials may sometimes require some calcination to improve their reactivity if their pozzolanic activity does not pass the ASTM C 618 criterion. The other prominent type is fly ash (FA) (ASTM C 618, Class F and C), which is the remnant of coal burning in thermal power plants. If the ash is rich in lime, it is called lignitic type (Type C). If the lime content is less than 10%, the ash is denoted as Type F (bituminous). Blast furnace slag (BFS) (ASTM C 989) is a byproduct of the steel processing industry with a high content of lime, silica and alumina. Silica fume (SF) (ASTM C 1240) is a by-product of the silicon and ferrosilicon industry. Due to its high amorphous silica content and

extreme fineness, SF is considered a super-pozzolanic material [11]. Fly ash and BFS have excellent record of experimental research and application in construction sites in many parts of the world. Though SF lacks long-term data, its superior performance in minimizing reinforcement corrosion has made it a “must” ingredient to produce superior quality concrete [11].

Chindaprasirt et al. [14] studied the influence of fly ash fineness on strength and other durability properties of hardened mortar. For all the mixes a constant flow of 110% was maintained. It was found that in general using fly ash helps reducing w/c ratio, as its particles are spherical they help reduce friction between particles and improve workability. With low w/c ratio than that of OPC mix, mortar prepared with fly ash as a partial replacement of cement showed compressive strengths which were comparable with OPC at 90 days; although, early age strength is always lower then OPC. Also, the courser type of fly ash used in this studied required more water than OPC to get the required flow of 110%, showed very low compressive strength at 90 days. This strength was far less than that of OPC. Fly ash-OPC concrete specimens also show lower drying shrinkage and less expansion due to sulfate attack.

Miletic et al. [15] took slag, natural pozzolan and fly ash and ground them with OPC clinker to produce blended cements in lab and reported that the compressive strength with these additives improved at later stages, but only 30% replacement of cement clinker with tuff matched strength of OPC at 180 days and later ages. Also, it was reported that the leaching of cement was improved tremendously with these replacements but the depth of carbonation was reported to be higher than OPC for all pozzolanic replacements.

2.2 Natural Pozzolan

Natural pozzolan has been utilized in many countries throughout the world where it is available as a local material. Some other countries have imported this material for the technical advantage. Most of the studies have shown that the properties of concrete have improved by the incorporation of natural pozzolan. Recently, Ghirci et al. [16] have evaluated the properties of ternary cements incorporating natural pozzolan. Mortar prisms in which Portland cement was replaced by up to 30% natural pozzolan were tested in flexure and compressive strength after 2, 7, 28, and 90 days of curing. It was reported that the use of ternary blended cement improved the early age and the long-term compressive and flexural strengths.

Mouli and Khelafi [17] studied the potential of using pozzolan from a natural source in Algeria as a pozzolanic material. In order to gain more knowledge on the efficiency of pozzolan concrete, six concrete mixtures: one mixture only with Portland cement (control) and five mixtures with 10%, 20%, 30%, 40%, and 50% of replacement of cement by pozzolan were tested. Crushed pozzolan was used as lightweight aggregate and natural sand was used in all mixes to produce a lightweight aggregate concrete. Fresh concrete mixtures were tested for workability and density. The hardened concrete specimens were tested for compressive strength, splitting tensile strength, and flexural strength after 3, 7, 28, 90 and 365 days. A total cementitious materials content of 400 kg/m^3 was maintained invariant in all the concrete mixtures. The concrete mixtures were designed for a constant workability expressed with a measured slump of 5±1 cm. It was

reported that the use of 20% pozzolan produced the highest strength increase at 365 days among the mixtures that were cast with some percentage of OPC replaced by natural pozzolan.

Rahmani and Ramazanianpour [18] studied the effect of binary cement replacement materials on sulfuric acid resistance of dense concrete. Four concrete groups were investigated. The first group contained Type II Portland cement as a control mix and the second group contained cement and superfine quartz powder as filler with particle size less than 16 μm. The third group included three different mixtures containing cement and cement material replacements including 8% silica fume, 20% trass and pumice as natural pozzolans. Finally, three mixtures were designed in the forth group based on binary cement replacement materials containing cement with 15% natural pozzolans and 8% silica fume or 10% trass and 10% pumice and super-fine filler. The dense packing of siliceous aggregates and cementitious materials was used to achieve the highest density of concrete. Specimens were immersed in sulfuric acid with pH = 1.0. They were periodically examined for appearance, measured for mass change and tested in compression and flexure up to 180 days. It was reported that the weight loss was higher for the mortar specimens with less water/binder ratio then specimens prepared with higher water/binder ratio, when immersed in sulfuric acid solutions. There is, however, an optimum cementitious material content for each mixture. The performance of mortar and concretes containing trass and ultra-fine filler was better than the other mixes. Mortar and concrete specimens with silica fume did not perform well in sulfuric acid environments.

Najimi et al. [19] investigated the effects of tuff natural pozzolan on the properties of Portland cement concrete. The durability and mechanical properties of concrete made by these cements were studied. It was found that using the natural pozzolan does not significantly affect the mechanical properties of the Portland cement concrete. Furthermore, the natural pozzolan-containing concrete did not perform well in freeze and thaw. Considerable improvements in depth of water penetration, expansion due to alkali-silica reaction, alkali reactivity and a slight improvement in chloride ion permeability were observed.

Siad et al. [20] studied the effect of mineral admixtures on resistance to sulfuric and hydrochloric acids of self-compacting concrete (SCC). The SCC specimens were prepared with natural pozzolan, and immersed for up to 12 weeks in sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) solutions. The results were compared with those from a control concrete and other SCCs prepared with fly ash and limestone filler. In total, 12 formulations were tested. The resistance of SCC to the acid attack was evaluated by measuring mass and compressive strength loss. Scanning electron microscope (SEM) and X-ray diffraction (XRD) analyses were used to better understand the kinetics of deterioration of each type of concrete. It was reported that the SCC prepared with natural pozzolan behaved well under both sulfuric and hydrochloric acid mediums.

Jamal and Asim [21] studied the properties of pastes, mortars and concretes containing natural pozzolan. Results show that initial strength of concretes and mortars with pozzolan were always less than that of concrete and mortars without pozzolans but at

later stages both strength matches. Addition of pozzolan in cement increases the soundness of concrete. Further, mortars prepared with the addition of natural pozzolan showed higher shrinkage but it was within the specified limit.

Colak [22] studied the characteristics of pastes prepared from Portland cement and natural pozzolan and found that the strength of pastes with natural pozzolan and Portland cement is found to be less than that of pastes from Portland cement without natural pozzolan although in one case in pozzolan/cement ratio of 20:80 with curing period of 180 days the strength of blended cement paste is almost equal to that of paste of ordinary Portland cement. In all cases the resistance to sulfate attack of blended cement pastes was less than that of ordinary Portland cement paste.

Turanli and Uzal [23] examined the characteristics of laboratory produced blended Portland cement concrete using natural pozzolan in the tune of 55% by weight of cement with a w/c ratio of 0.45 and its effect on the properties of concrete produced was studied. The compressive strength of the blended cement concretes at ages up to 28 days was lower than that of reference Portland cement concrete but at 91 days, the results were similar. It also reduced the alkali-silica expansion.

Pekmezci and Akyuz [24] worked on the optimization of natural pozzolan for maximum compressive strength and found that the optimum pozzolan/cement ratio to achieve maximum strength is 0.28; also with same amount of pozzolan used, the maximum strength is associated with highest cement content.

Najimi et al. [25] used zeolite as a natural pozzolan in concrete with 15% and 30% replacement of cement and studied its effects on compressive strength and durability properties of concrete. They reported that the compressive strength for both mixes with natural pozzolan was less than that of control OPC mix at all stages and 15% replacement performed better than 30% replacement. Also, it was reported that with the partial replacement of OPC with natural pozzolan, the shrinkage and corrosion was reduced. Since it was reported that natural pozzolans do not perform as good as other materials; they need to be activated by using mechanical or chemical methods.

2.3 Improving Performance of Natural Pozzolan

Ghrici et al. [16] conducted a study in which twelve mixes were cast with natural pozzolan and limestone filler used as a partial replacement to OPC in different percentages by mass. It was reported that at 28 days compressive strength of all the mixes was less than control mix of OPC. At 90 days the compressive strength for mix with 20% natural pozzolan and 10% limestone filler is higher than OPC. Ternary mixes exhibited better chloride ion permeability performance than OPC. Mixes with partial replacement of OPC by natural pozzolan performed well in acid attack of hydrochloric acid.

Jamal and Asim [21] studied the properties of pastes, mortars and concretes containing natural pozzolan. Results show that the initial strength of concretes and mortars with pozzolan were always less than that of concrete and mortars without pozzolans but at later stages both strength matches. With the increase in fineness of natural pozzolan, the strength also increases as the reactivity increases. Addition of pozzolan in cement

increases the soundness of cement. Further, mortars prepared with the addition of natural pozzolan showed higher shrinkage but it was within the specified limit.

Day and Shi [26] studied the effect of fineness of pozzolan on the strength of lime-natural pozzolan cement pastes. Natural pozzolan from Bolivia was grounded to different fineness with lime with a mass ratio of 80:20. In some mixes, some activators were also used to enhance the strength development. Results show that increasing the fineness was effective in increasing the reactivity of natural pozzolan and there is a linear correlation between Blaine fineness of pozzolan and strength of pastes at all ages but the effect of fineness was most profound at early ages, Further, the activators used were more affective when added with finer pozzolan.

In another study, Shi and Day [27] used the same mix of natural pozzolan from Bolivia with lime with a mass ratio of 80:20 and studied the effect of chemical, mechanical and thermal activation on performance of lime-pozzolan. Mechanical activation was achieved by prolonged grinding of lime-pozzolan while chemical activation was achieved by introducing 4% sodium sulfate into mix. Mixing and curing temperatures were elevated to achieve thermal activation. They reported that all the methods accelerated the pozzolanic reaction within first three days. Ultimate compressive strength did not increase significantly due to mechanical activation and thermal activation decreased the ultimate strength. Chemical activation produced the maximum strength increase among all three methods.

Habert et al. [28] worked on thermal treatment of concrete prepared with ordinary Portland cement and natural pozzolans as cementing material and found that for different compositions of pozzolans, there is different optimum temperature which maximizes the pozzolanic activity. Results show that pozzolanic activity of natural pozzolan increases with thermal treatment of concrete. Results also show that the concretes with some percentage of OPC being replaced with natural pozzolan give higher strength than concretes where this percentage is replaced by an inert material. Formation of secondary hydration product is also confirmed using X-Ray diffraction and SEM techniques.

Zelic et al [29] studied the properties of ternary mixes of OPC-lime-silica fume and prepared mixes with 15% replacement of OPC with limestone. Silica fume was added in amounts 0, 2, 5, 8, 11 and 15%. It was reported that addition of limestone as a partial replacement of OPC increased the total porosity of mortars but these pores were not well connected and thus permeability was not affected. Also, with the inclusion of a pozzolanic material; in this case silica fume improved the porosity tremendously.

Uzal et al. [30] studied and compared the pozzolanic activity of natural pozzolan-lime system with silica fume and fly ash. It was reported that free lime consumption within mortars for lime-pozzolan was higher than fly ash and just about equal to the consumption of silica fume. Although the consumption of free lime by lime-pozzolan system was better, still the 28 days compressive strength was significantly lower than mortars with fly ash and silica fume. This is because of the micro structural difference in the hydrations products as natural pozzolans are mostly crystalline whereas for silica fume and fly ash, they are non-crystalline pozzolanic materials.

2.4 Durability Properties of Blended Cements

2.4.1 Sulfate Attack

Ghrici et al. [16] conducted a study in which 12 mixes were prepared with 30% natural pozzolan and limestone filler used as a partial replacement to OPC in different percentages by mass. Samples were exposed to 5% sodium sulfate and 5% magnesium sulfate separately and used expansion as well as weight loss as failure criteria. It was reported that all the specimens in sodium sulfate solution showed higher expansion than their respective specimens in magnesium sulfate solution. The results were vice versa in the case of weight loss and samples in magnesium sulfate solution lost more weight than their respective specimens in saosium sulfate solution. Also, specimens with 30% natural pozzolan replacement were reported to have near about half as much expansion as in control plain OPC specimens. Other observation included that inclusion of 15% lime in the mix did not affect the expansion of specimens and even natural pozzolan was unable to reduce expansion in OPC-lime-natural pozzolan system. Regarding weight loss OPC control mix showed most weight lost mixes with 15% lime, 30% natural pozzolan replacements and ternary system of OPC-lime-natural pozzolan showed nearly same amount of weight loss which was less than control mix.

Colak [22] studied the characteristics of pastes prepared from Portland cement and natural pozzolan and found that in all cases the resistance to sulfate attack of blended cement pastes was less than that of ordinary Portland cement paste.

Rodriguez and Uribe [34] conducted test according to ASTM 1012 to test performance of natural pozzolan blended cement concrete under sulfate attack. They used eight different pozzolans available in Mexico and found that pozzolans associated with high pozzolanic activity, when blended with Type I cement give more sulfate resistance than Type V cement concretes.

Kilinckale [35] studied the strength loss of pozzolan cement mortars after exposure in magnesium sulfate solution and found that all pozzolans have showed pozzolanic activity. Also, all the mortars with pozzolans showed higher durability than OPC Type I cement mortars.

Hossain and Lachemi [36] studied the performance of volcanic ash and pumice based blended cement concrete in mixed sulfate environment. Two series of mixes were prepared; one with w/c ratio of 0.35 and other with w/c ratio of 0.45. In each series, two control mixes were prepared one with OPC Type I cement and other with sulfate-resistant Type V cement. Other mixes included 20% replacement of Type I and Type V cement by volcanic ash and volcanic pumice. They prepared bar specimens and used weight loss as a failure criterion. At 28 days, all pozzolan blended cement concretes showed lower strength and lower porosity than two control mixes. Differential scanning calorimetry showed that free lime content in blended cement concretes was less than that in the control mixes showing that the secondary hydration is taking place. Initially gain in weight was reported as the sulfate salts and expansive reaction products filled the pores and make the hardened matrix denser. It was also reported that up till 18 months blended

cement concretes performed almost same like both the control mixes. All the specimens prepared, with or without pozzolan showed nearly similar weight loss. The trends start to change at 48 months; the last observation, both Type I and Type V cement concrete performed far better than blended cement concretes. This is because there is no calcium hydroxide left to react which was consumed by pozzolanic ash and pumice and magnesium reacts directly with C-S-H to form soft low density, non-cementitious M-S-H. Lower water to cement ratio also showed higher weight loss values as it has less pores to accommodate reaction product which leeches out resulting in greater weight loss.

Neville [37] in his review article discussed about the factors involved in the deterioration of concrete due to sulfate ions. He concluded that there is no unique answer to sulfate attack and its prevention, as the mechanism of sulfate attack is different with sodium, calcium, or magnesium being the associated cation with sulfate anion. It was made clear that dry salts do not harm concrete because it's the solution that is deleterious which transports the salts within the concrete. Regarding the w/c ratio, it was concluded that it's the quality of concrete which is more important. If concrete is not dense, lowering the w/c ratio may increase the sulfate attack. Sulfate resistant cement is beneficial if the ingressing sulfates are calcium and sodium sulfates and do not affect the performance to a great extent if magnesium sulfate is the environment. With his review, the author also concluded that low C_3S to C_2S ratio cannot guarantee sulfate resistance property to any cement. Although carbonation has its own menace but carbonation of concrete specimens prior to exposure to sulfate environment reduces the buildup of sulfates in concrete.

Sahmaram et al. [38] studied the effects of mix composition and w/c ratio on sulfate resistance of blended cements. Specimens of mortar were prepared with OPC Type I and Type V cements as control, binary mixes of OPC-NP and OPC-FA and ternary mixes of OPC-NP-FA. These specimens were exposed to 5% sodium sulfate solution for 78 weeks. It was reported that Type V (sulfate resistant cement) gave highest strength at all ages among all the mixes and did not show significant strength loss. Also, lowering the w/c ratio improved the performance to mixes in sulfate environment and less expansion was observed in lower w/c ratio mixes. Performance of fly ash was reported to be better than natural pozzolan.

Hekal et al. [39] studied magnesium sulfate attack on blended cement pastes. Silica fume and slag were used as partial replacement to cement and w/c ratio of 0.3 was used for all mixes. Further, three different exposure schemes were used; at room temperature, at 60°C and at 60°C with wetting and drying cycles. All the schemes were of 10% magnesium sulfate solution. It was reported that the addition of silica fume did not show any improvement in sulfate resistance of cement pastes when replaced OPC by 10% and 15%. OPC, when replaced with 40% slag showed most improvement in sulfate resistance. Also, it was reported that wetting and drying cycles accelerates sulfate attack.

Al-Amoudi [40] studied the behavior of blended cement concretes in sulfate environments. It was reported that deterioration of concrete specimens was superficial and bulk of the concrete maintains its dense micro-structure when exposed to magnesium sulfate environment. It was reported that all the blended cement concretes showed higher

strength reduction than OPC concretes when exposed to magnesium sulfate solutions; this is primarily due to the consumption of CH content by pozzolanic reaction. Further, blended cement concretes exhibit superior performance in sodium sulfate environment and showed less expansion and weight loss. It was also reported that the concomitant presence of chlorides with the sulfate ions tends to mitigate sodium sulfate attack due to the enhanced solubility of gypsum and ettringite thereby inhibiting their expansive characteristics. In magnesium sulfate exposures, the chlorides alleviate the gypsum attack in a way similar to that in NS environments. However, the chloride ions do not significantly affect the attack of magnesium sulfate on C–S–H. As a consequence, magnesium sulfate attack on blended cements exposed to sulfate–chloride environments progresses unhindered by chlorides.

2.4.2 Chloride Diffusion and Reinforcement Corrosion

Ghirci et al. [16] evaluated the properties of ternary cements incorporating natural pozzolan. Mortar prisms in which Portland cement was replaced by up to 30% natural pozzolan were tested in flexure and compressive strength after 2, 7, 28, and 90 days of curing. Some specimens were immersed in salt solutions and chloride permeability was determined. It was reported that the use of ternary blended cement improved chloride ions penetration resistances as compared with OPC control mix.

Fajardo et al. [41] studied the corrosion of steel rebar embedded in mortars prepared with natural pozzolan and exposed to chloride solution. Natural pozzolan at 0%, 10% and 20% by mass of normal Portland cement was used as a partial substitute of normal Portland cement in reinforced mortar specimens. Compressive strength, corrosion potential,

polarization resistance, electrical resistivity, and chloride content of the mortars were determined in order to characterize the physical, mechanical, electrical, and electrochemical behavior of the mortar as well as the embedded steel. It was found that the use of pozzolan has resulted in a significant increase in mortar resistivity and corrosion initiation time for the same cover depth.

2.4.3 Carbonation

Kritsada and Lutz [42] studied the effect of curing period on carbonation resistance of high pozzolanic material blended cements. Mortar of 25 and 50% replacement of OPC with fly ash and blast furnace slag cement (Type III) were studied. Samples were submerged under water for 3, 7 and 28 days for curing. After the curing ended, the samples were exposed to accelerated carbonation for 9 weeks. It was reported that in all cases the depth of carbonation for all the blended cements was higher than that of OPC for all periods of curing. 25% replacement of OPC with fly ash showed almost double the carbonation depth than OPC at the end of 9 week exposure. 50% replacement was even higher.

Khan and Lynsdale [43] studied the effect of adding different percentages of silica fume in mixes as a partial replacement of OPC, on carbonation resistance of cement. Just after demoulding the samples were kept in a mist room with 98% RH for two years where the samples were cured and exposed to natural carbon dioxide environment simultaneously. They reported that with the increase in silica fume content, the depth of carbonation also increased.

Jones et al. [44] studied ternary blended cements incorporating different percentages of silica fume in OPC-fly ash blend. Specimens were cast and cured under water for 28 days. After curing they were exposed to accelerated carbonation environment. It was reported that with the increase in silica fume content, the depth of carbonation also increased. Even, without the inclusion of silica fume the blend of OPC-fly ash showed higher depths of carbonation than that of OPC.

Borges et al. [45] studied carbonation of calcium hydroxide and C-S-H in blended cements containing 75 and 90% replacement of OPC by blast furnace slag (BFS). Specimens were cured for 90 days and then exposed to highly accelerated carbonation for 21 days. They reported that the carbonation depth increased with the increase in BFS content. Also, the amount of C-S-H calcinating depends up on the amount of calcium hydroxide present in the hydrated pastes before carbonation starts. Less calcium hydroxide, which is the case with high BFS content (calcium hydroxide being consumed by pozzolanic reaction), there is less buffer for C-S-H to calcinate.

Papadakis [46] studied the resistance of blended cements to carbonation. He used silica fume and high and low calcium fly ash in different dosages as a partial replacement of OPC. The specimens were submerged under water and cured for 1 year. After the curing the specimens were exposed to accelerated carbonation for a period of 100 days. He reported that OPC performed better than all blended cements. Also, high calcium fly ash performed better than silica fume and low calcium fly ash which were high in siliceous material and low on calcium content.

CHAPTER 3

METHODOLOGY OF RESEARCH

3.1 Experimental Program

The objective of this research was to study the compressive strength and durability properties of concrete prepared with locally available natural pozzolan used as a partial replacement of cement. Also, activation techniques popularly used (i.e. chemical, mechanical and physical) to increase the reactivity of the selected pozzolan were studied. Both the compressive strength and the durability performance of the concrete were evaluated. The reactivity was evaluated by measuring water penetration, drying shrinkage, chloride diffusion, sulfate attack, salt weathering, carbonation and reinforcement corrosion. Figure 3.1 shows the experimental program.

3.2 Materials

3.2.1 Cements and Blending Materials

ASTM C 150 Type I Portland cement, having a specific gravity of 3.15, was utilized in all the concrete mixes, except in two mixes where NP blended OPC was utilized.

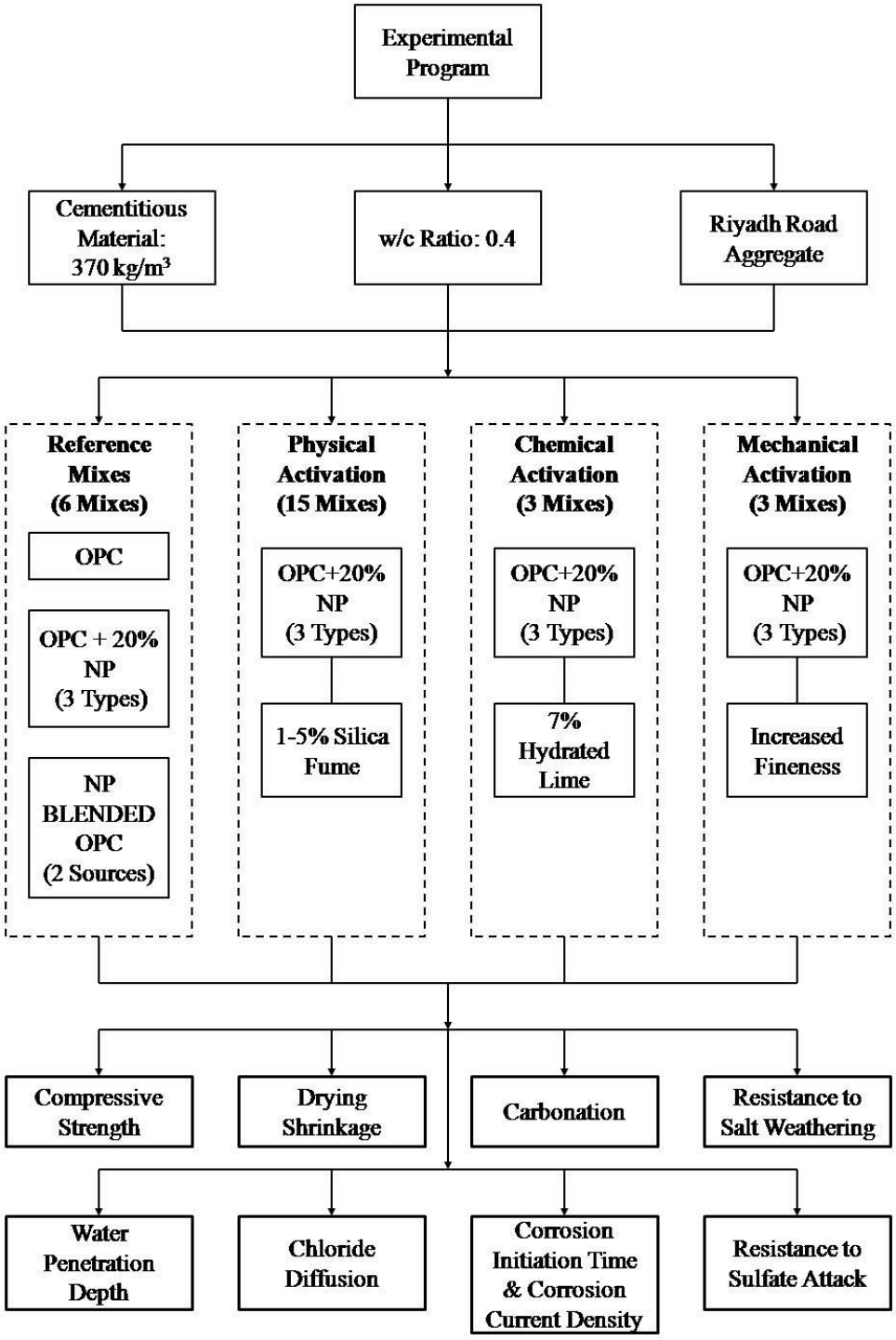

Figure 3-1 Flow chart of Experimental Program

Natural pozzolan from three sources having two grades of fineness, silica fume and hydrated lime was used as replacement of Portland cement. Natural pozzolan 1 was supplied by Super Barkani a local supplier of natural pozzolan. Similarly, natural pozzolan 2 and 3 were supplied by Al-Ghahtani and Abu-Arish companies, respectively. All three types of natural pozzolan came from the western region of Saudi Arabia. Pozzolana cement 1 is a natural pozzolan blended cement product of Arabian cement factory, Jeddah while pozzolana cement 2 is a product of Tabuk cement factory, Tabuk. Table 3.1 shows the chemical composition of the Portland cement while Table 3.2 shows the chemical composition of blending materials. Table 3.3 shows the Blaine fineness of natural pozzolan from three sources along with the average particle size determined by laser particle analysis technique.

Table 3-1: Chemical Composition of Cements.

Constituent (Wt %)	**OPC**	**Pozzolana Cement 1**	**Pozzolana Cement 2**
CaO	64.35	52.8	53.5
SiO_2	22	26.2	25.6
Al_2O_3	5.64	7.61	6.92
Fe_2O_3	3.8	6.36	6.12
K_2O	0.36	0.46	0.51
MgO	2.11	3.51	3.97
Na_2O	0.19	0.15	0.13
Equivalent alkalis (Na_2O + 0.658K_2O)	0.42	0.45	0.46
Loss on ignition	0.7	1.68	1.71
C_3S	55	57	58
C_2S	19	22	21
C_3A	7	8	7
C_4AF	10	11	11

Table 3-2: Chemical Composition of Blending Materials

Constituent (Wt %)	Natural Pozzolan 1	Natural Pozzolan 2	Natural Pozzolan 3	Natural Pozzolan 1 (Fine)	Natural Pozzolan 2 (Fine)	Natural Pozzolan 3 (Fine)	Silica Fume	Hydrated Lime
SiO_2	41.47	40.23	43.91	41.42	40.27	43.98	92.5	3.65
Al_2O_3	12.81	14.51	16.22	12.85	14.49	16.19	0.72	0.77
Fe_2O_3	17.53	17.98	11.64	17.61	18.01	11.71	0.96	0.31
CaO	8.76	7.44	9.36	8.77	7.48	9.31	0.48	94.2
MgO	8.9	8.3	8.8	8.92	8.26	8.85	1.78	1.02
K_2O	0.82	0.89	0.79	0.82	0.89	0.79	0.84	-
Na_2O	3.4	3.6	3.1	3.4	3.6	3.1	0.5	-
L.O.I	1.5	1.6	1.4	1.5	1.6	1.4	1.55	22.84

Table 3-3: Fineness Parameters of Natural Pozzolan

Parameter	Natural Pozzolan 1	Natural Pozzolan 2	Natural Pozzolan 3	Natural Pozzolan 1 (Fine)	Natural Pozzolan 2 (Fine)	Natural Pozzolan 3 (Fine)
Surface Area, **m^2/kg**	426	442	394	784	801	773
Avg. Dia Particle, **μm**	35.38	32.63	37.01	20.36	19.57	21.22

3.2.2 Aggregates

Three aggregate sizes of 12.5 mm (½ inch), 4.75 mm (3/16 inch), and 2.36 mm (3/32 inch) crushed limestone from Riyadh Road were used in all the concrete mixtures as coarse aggregate. The grading of the coarse aggregates was selected conforming to ASTM C 33 size # 57 and shown in Table 3.4. Absorption and specific gravity of the coarse aggregates were 1.1% and 2.6, respectively. For the fine aggregate dune sand, with water absorption of 0.6% and specific gravity of 2.56, was used.

Table 3-4: Grading of Coarse Aggregates

Sieve Opening, mm (inch)	% Retained	Cumulative (% Retained)	% Passing	ASTM C 33 (# 57 Grading)
38 (1½)	0	0	100	0
25 (1)	0	0	100	0-5
19 (3/4)	0	0	100	-
13 (1/2)	70	70	30	40-75
10 (3/8)	0	70	30	-
5 (3/16)	25	95	5	90-100
2.5 (3/32)	5	100	0	95-100

3.3 Concrete Mixture Design

Concrete mixtures were designed and the proportioning of materials was carried out on a weight basis. All the concrete mixtures were prepared with a cementitious materials content of 370 kg/m^3, effective water to cementitious materials ratio of 0.4, and a coarse to total aggregate ratio of 0.62. All the afore-mentioned parameters were kept invariant in all the concrete mixtures. A superplasticizer was added to the concrete mixtures to obtain a constant slump of 100 ± 25 mm. Table 3.5 shows the details of the weight

proportioning of mixtures investigated while Table 3.6 shows the weights of the materials for these mixtures and Table 3.7 shows the weights of the aggregates used in all the 28 concrete mixtures prepared in this study.

3.3.1 Reference Concrete Mixtures

Literature review indicates that the optimum dosage (replacement by weight of OPC) of natural pozzolan generally falls within the range of 20 to 30% replacement of Portland cement [27, 28], each of the three Saudi natural pozzolans (NPs) was added to OPC in 20% dosages by replacement of cement. Therefore, the following four reference mixes were prepared:

Mix #1: 100% Type I cement (OPC); and

Mix #2 through Mix #4: The three blended NP-OPC cements with 20% NP dosage for each pozzolan.

Also, in addition to the four mixtures (Mix #1 to Mix #4), the following three more reference mixtures were prepared:

Mix #5: 92.5% OPC + 7.5% silica fume (SF);

Mix #6: NP-OPC blended cement from the Arabian Cement Company (Jeddah); and

Mix #7: NP-OPC blended cement from Tabuk Cement Company (Tabuk).

Altogether, there were seven reference mixtures. Mix # 1 i.e. 100% Type I cement (OPC) served as a reference for the mixtures which are discussed below. Along with that, Mix # 1 also served as a reference for the remaining 6 reference mixtures.

3.3.2 Improving the Performance of NP-OPC Using Silica Fume

Silica fume was added to the three reference NP-OPC mixtures (Mix #2 to Mix #4) in the dosages; 1, 2, 3, 4, and 5% by weight of cement to improve the performance of NP-OPC mixtures (i.e. physically). With the addition of five silica fume dosages to each of Mix #2 to Mix #4, fifteen (15) mixtures (Mix #8 and Mix #22) were cast.

3.3.3 Improving the Performance of NP-OPC Using Hydrated Lime

Hydrated lime [$Ca(OH)_2$] was used to activate the hydration reactions (i.e. chemically) of the three reference NP-OPC cements. The optimum dosage of HL, i.e. 7%, was used to prepare three more concrete mixes (Mix #23 and Mix #25).

3.3.4 Improving the Performance of NP-OPC by increasing the fineness of NP

The three natural pozzolans were pulverized to one additional fineness (in addition to the existing one). The particle size used was based on the crushers available in the Saudi market. Hence, three (3) more mixes were cast to assess the role of fineness of NP on the performance of NP-OPC mixes. Mix #26 and Mix #28 were cast as per this scheme.

Table 3-5: Details of Control and Blended Cement Concrete Mixtures Proportions*.

Mix #	OPC/ NP-OPC, %	NP 1, %	NP 2, %	NP 3, %	NP 1, (Fine) %	NP 2, (Fine) %	NP 3, (Fine) %	SF, %	HL, %
M 1	100	--	--	--	--	--	--	--	--
M 2	80	20	--	--	--	--	--	--	--
M 3	80	--	20	--	--	--	--	--	--
M 4	80	--	--	20	--	--	--		--
M 5	92.5	--	--	--	--	--	--	7.5	--
M 6	100	--	--	--	--	--	--	--	--
M 7	100	--	--	--	--	--	--	--	--
M 8	79	20	--	--	--	--	--	1	--
M 9	78	20	--	--	--	--	--	2	--
M 10	77	20	--	--	--	--	--	3	--
M 11	76	20	--	--	--	--	--	4	--
M 12	75	20	--	--	--	--	--	5	--
M 13	79	--	20	--	--	--	--	1	--
M 14	78	--	20	--	--	--	--	2	--
M 15	77	--	20	--	--	--	--	3	--
M 16	76	--	20	--	--	--	--	4	--
M 17	75	--	20	--	--	--	--	5	--
M 18	79	--	--	20	--	--	--	1	--
M 19	78	--	--	20	--	--	--	2	--
M 20	77	--	--	20	--	--	--	3	--
M 21	76	--	--	20	--	--	--	4	--
M 22	75	--	--	20	--	--	--	5	--
M 23	73	20	--	--	--	--	--	--	7
M 24	73	--	20	--	--	--	--	--	7
M 25	73	--	--	20	--	--	--	--	7
M 26	100	--	--	--	20	--	--	--	--
M 27	100	--	--	--	--	20	--	--	--
M 28	100	--	--	--	--	--	20	--	--

* All the weight proportions are related to the weight of Cement (OPC).

Table 3-6: Weights of materials in the concrete mixtures investigated.

Mix #	w/c	OPC/ PBC* kg/m^3	NP 1 kg/m^3	NP 2 kg/m^3	NP 3 kg/m^3	NP 1 (Fine) kg/m^3	NP 2 (Fine) kg/m^3	NP 3 (Fine) kg/m^3	SF kg/m^3	HL kg/m^3
M 1	0.4	370	--	--	--	--	--	--	--	--
M 2	0.4	296	74	--	--	--	--	--	--	--
M 3	0.4	296	--	74	--	--	--	--	--	--
M 4	0.4	296	--	--	74	--	--	--	--	--
M 5	0.4	342.3	--	--	--	--	--	--	27.75	--
M 6	0.4	370	--	--	--	--	--	--	--	--
M 7	0.4	370	--	--	--	--	--	--	--	--
M 8	0.4	292.3	74	--	--	--	--	--	3.7	--
M 9	0.4	288.6	74	--	--	--	--	--	7.4	--
M 10	0.4	284.9	74	--	--	--	--	--	11.1	--
M 11	0.4	281.2	74	--	--	--	--	--	14.8	--
M 12	0.4	277.5	74	--	--	--	--	--	18.5	--
M 13	0.4	292.3	--	74	--	--	--	--	3.7	--
M 14	0.4	288.6	--	74	--	--	--	--	7.4	--
M 15	0.4	284.9	--	74	--	--	--	--	11.1	--
M 16	0.4	281.2	--	74	--	--	--	--	14.8	--
M 17	0.4	277.5	--	74	--	--	--	--	18.5	--
M 18	0.4	292.3	--	--	74	--	--	--	3.7	--
M 19	0.4	288.6	--	--	74	--	--	--	7.4	--
M 20	0.4	284.9	--	--	74	--	--	--	11.1	--
M 21	0.4	281.2	--	--	74	--	--	--	14.8	--
M 22	0.4	277.5	--	--	74	--	--	--	18.5	--
M 23	0.4	270.1	74	--	--	--	--	--	--	25.9
M 24	0.4	270.1	--	74	--	--	--	--	--	25.9
M 25	0.4	270.1	--	--	74	--	--	--	--	25.9
M 26	0.4	296	--	--	--	74	--	--	--	--
M 27	0.4	296	--	--	--	--	74	--	--	--
M 28	0.4	296	--	--	--	--	--	74	--	74

* NP-blended Cement

Table 3-7: Weights of aggregates in each mix used in this investigation.

Mix	Coarse Aggregate (kg/m^3)				Fine
	1/2 "	# 4	# 8	Total	
M 1	823.9	294.3	58.9	1898.5	721.4
M 2	822.6	293.8	58.8	1895.5	720.3
M 3	822.6	293.8	58.8	1895.5	720.3
M 4	822.6	293.8	58.8	1895.5	720.3
M 5	820.0	292.8	58.6	1889.4	718.0
M 6	823.9	294.3	58.9	1898.5	721.4
M 7	823.9	294.3	58.9	1898.5	721.4
M 8	825.6	294.9	59.0	1902.4	722.9
M 9	828.6	295.9	59.2	1909.2	725.5
M 10	831.6	297.0	59.4	1916.1	728.1
M 11	834.5	298.1	59.6	1922.9	730.7
M 12	837.5	299.1	59.8	1928.8	733.3
M 13	825.6	294.9	59.0	1902.4	722.9
M 14	828.6	295.9	59.2	1909.2	725.5
M 15	831.6	297.0	59.4	1916.1	728.1
M 16	834.5	298.1	59.6	1922.9	730.7
M 17	837.5	299.1	59.8	1928.8	733.3
M 18	825.6	294.9	59.0	1902.4	722.9
M 19	828.6	295.9	59.2	1909.2	725.5
M 20	831.6	297.0	59.4	1916.1	728.1
M 21	834.5	298.1	59.6	1922.9	730.7
M 22	837.5	299.1	59.8	1928.8	733.3
M 23	843.5	301.2	60.2	1943.5	738.5
M 24	843.5	301.2	60.2	1943.5	738.5
M 25	843.5	301.2	60.2	1943.5	738.5
M 26	822.6	293.8	58.8	1895.5	720.3
M 27	822.6	293.8	58.8	1895.5	720.3
M 28	822.6	293.8	58.8	1895.5	720.3

3.4 Batching and Curing of Concrete Specimens

Concrete specimens were prepared and cured to carry out various tests planned in this investigation. Batching of each mix was proportioned by weight. Aggregates were initially sieved to obtain the required sizes. The concrete constituents were thoroughly

mixed in a revolving drum mixer for approximately three to five minutes to obtain uniform consistency. Super-plasticizer was added with different doses to enhance the workability and to keep the slump around 100 ± 25 mm. After mixing, the slump was measured then concrete was poured in the moulds in three layers. The moulds were then vibrated till complete consolidation was achieved, as indicated by a thin film of mortar appearing on the concrete surface. After casting, the specimens were covered with plastic sheet for 24 hours in the laboratory environment (22 ± 3 ^{0}C) to minimize the loss of mixing water. After 24 hours, the specimens were de-moulded and placed in a curing tank till the time of test. Table 3.8 summarizes the type and number of specimens prepared and tested.

Table 3-8: Details of concrete specimens cast and tested.

Property	Specimen size & shape	Test period, days	Test method	Specimens Tested
Compressive Strength	100 mm Cube	7, 14, 28, 90, 180 & 360	ASTM C 39	504
Water Permeability	150 mm Cube	28, 90 & 180	DIN 1048	252
Drying Shrinkage	25 x 25 x 300 mm prism	Long Term	ASTM C 157	84
Reinforcement Corrosion	75 x 150 mm cylinder	Every 30 days after curing	ASTM C 876 & LPRM	84
Chloride Diffusion	75 x 150 mm cylinder	180 & 360	Fick's second law of diffusion	56
Salt Weathering	75 x 150 mm cylinder	180 & 360	--	168
Sulfate Attack	75 x 150 mm cylinder	180 & 360	--	168
Carbonation	50 mm Cube	90 & 180	RILEM Standard CPC 18	168
Total Number of Specimens				1484

3.5 Laboratory Testing

3.5.1 Compressive Strength

Compressive strength was determined on 100 mm cube concrete specimens according to ASTM C 39 [47]. It is that value of the uniaxial compressive stress at which the material fails completely. The compressive strength was calculated by dividing the failure load by the cross-sectional area resisting the load and reported in Mega Pascal (MPa). The test

was done using a digital compression testing machine (MATEST) after 7, 14, 28, 90, 180 and 360 days of water curing. Three specimens were tested at each age and the average values are reported. Figure 3-2 shows the compression testing machine used for compression testing, while Figure 3-3 shows a concrete specimen after failure under compressive loads.

Figure 3-2: Compression testing machine used in this investigation

Figure 3-3: Concrete specimen failed under compressive loads

3.5.2 Water Penetration Depth

The water penetration test, which is most commonly used to evaluate the permeability of concrete, is specified by DIN 1048 [48]. In this test, 150 mm concrete cubes, after 28, 90 and 180 days of water curing, were dried under laboratory condition for 24 hour. They were then oven-dried in oven for 72 hours at 70^0 C and then cooled for 1 day in the laboratory condition.

Water under a pressure head of five bars was applied on one face of the specimen. This pressure was maintained for a period of 3 days. After the completion of the pressure application, the specimens were taken out and split open into two halves by placing the specimens between two wedges and applying a force using uniaxial compression testing machine. Specimens were split in such a way that top and bottom surfaces during

exposure remains top and bottom during splitting. The water penetration profile on the concrete surface was then marked and the maximum depth of water penetration in three specimens was recorded and considered as an indicator of the water permeability. Figure 3-4 shows the set-up used to determine the water penetration depth while Figure 3-5 shows a concrete sample after split. Table 3-9 represents the classification of water penetration according to The Concrete Society (1987).

Figure 3-4: Water Penetration Depth Test Set-up

Figure 3-5: Concrete Specimen Showing Penetration Profile

Table 3-9: Assessment of concrete according to water penetration depth [The Concrete Society, 1987].

Depth of penetration	Permeability
Less than 30 mm	Low
30 –60 mm	Moderate
More than 60 mm	High

3.5.3 Drying Shrinkage

Shrinkage is the reduction in the volume of concrete caused mainly by the loss of water due to evaporation from a freshly-hardened concrete exposed to air. Shrinkage may result in cracking of restrained concrete members. Mortar specimens of 25 x 25 x 300 mm were prepared for determining the drying shrinkage according to ASTM C 157 [49]. These mortar specimens were prepared with a water to cement ratio of 0.45 and sand to cementitious material ratio of 2.75. These specimens were water cured for 28 days. After the curing period the specimens were taken out and the initial length was noted. Lengths of the same specimens were noted on different intervals up to 210 days. The intervals between the readings were shorter at the initial age and comparatively longer at later age. Three specimens were tested and the average values were reported. Set-up on which the shrinkage is measured is shown in Figure 3-6. Set-up includes a LVDT connected to a data logger, a smooth base and a frame that helps to keep the specimen perfectly vertical

and stable during the test. A standard bar of known length is first used to initialize the test set-up. Then, the specimen is placed in and the length is read.

Figure 3-6: Set-up for Measuring Drying Shrinkage

3.5.4 Chloride Diffusion

The chloride diffusion was determined after 28 days of water curing. After this curing period, the specimens were allowed to dry for a week and then they were coated with an epoxy resin all over leaving one circular flat surface (top) uncoated. It is expected that uniaxial (i.e., one dimensional) diffusion of chloride would occur through the uncoated surface. The coated specimens were immersed in a 5% sodium chloride solution. After six months and then after 12 months period, the specimens were cleaned and dried to remove the surface moisture and thin slices of concrete were obtained at 5, 15, 25, 35, 45

and 75 mm by dry cutting. The slices were crushed and ground to a fine powder passing through ASTM No. 100 sieve.

In order to determine the total chloride concentration, three grams of the powder was dissolved in hot mixture of 3 ml concentrated nitric acid and 47 ml distilled water. The solution was kept in a shaker for 24 hours and thereafter, the specimen was filtered and the filtrate was diluted to 100 ml. A 0.2 ml sample is then taken from this diluted mixture and added to 9.8 ml distilled water, along with 2 ml mercuric theocynite and 2 ml of ferric aminosulfate. These chemicals react with chlorides in the sample and change the color of the mixture. This change in color depends up on the concentration of chlorides and can be detected by spectrophotometer. A small amount of this mixture is then taken into a test tube and is placed inside a spectrophotometer. The spectrophotometer gives an index which signifies the translucence of the sample. This index is calibrated to give chloride concentration. The chloride concentrations were plotted against the concrete depth for each specimen. The chloride diffusion profile was utilized to determine the coefficient of chloride diffusion according to Fick's second law of diffusion [50]. The solution of Fick's second low for a semi-infinite domain with a uniform concentration of C_S at the surface (x=0) that is as follows:

$$C_X = C_S \quad [1 - \text{erf}\{x / \sqrt{2tD}\}] \qquad (3.1)$$

Where:

C_x is the chloride concentration at depth x, %.

C_s is the chloride concentration at depth x, %.

x is the depth from concrete surface, cm

t is the time in seconds, and

D is the effective chloride diffusion coefficient, cm^2/s.

3.5.5 Time to Initiate Reinforcement Corrosion

After 28 days of water curing, the reinforced concrete specimens (75 mm in diameter and 150 mm high with a centrally placed 12 mm diameter steel bar) were partially submerged (40 mm) in 5% NaCl solution. The corrosion potentials on steel in these specimens were regularly measured using saturated calomel electrode (SCE) in accordance with ASTM C 876 [52]. The time needed to cross the –270 mV SCE in the potential–time curves was recorded as at this point there is 90% probability for initiation of reinforcement corrosion. Table 3-10 indicates the possibility of reinforcement corrosion, as reported in ASTM C 876 [51] while Figure 3-7 shows the corrosion potential measurement set-up.

Table 3-10: Probability of occurrence of reinforcement corrosion.

Open circuit potential (OCP) values		Corrosion condition
(mV vs. SCE)	**(mV vs. CSE)**	
< -426	< -500	Severe corrosion
< -276	< -350	High (<90% risk of corrosion)
> -125 but < -276	> -200 but < -350	Intermediate corrosion risk
> -125	< -200	Low(10% risk of corrosion)

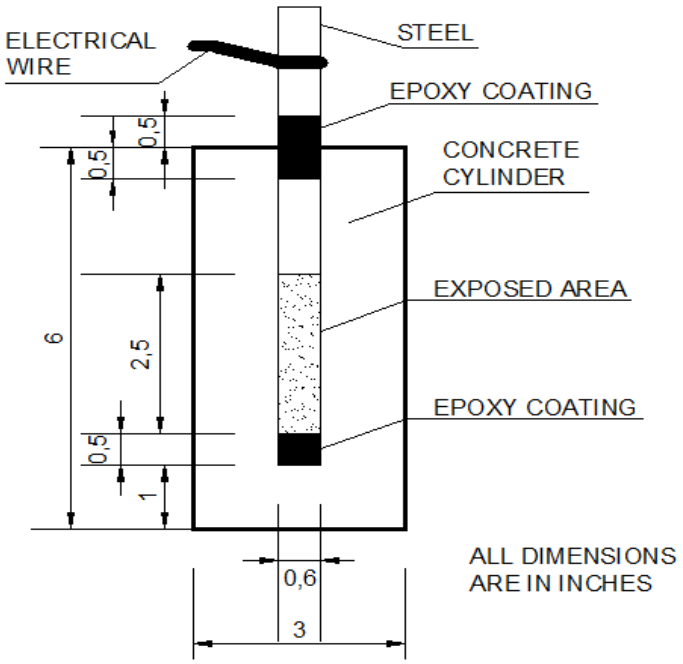

Figure 3-7: Corrosion Potential Measurement Setup.

3.7.6 Corrosion Current Density

The corrosion current density measurements provide an indication of the rate at which the reinforcement corrosion is progressing. This information is of great importance in knowing the extent of corrosion damage and in predicting the remaining service life, which is useful in taking decisions regarding the repair and rehabilitation works. The corrosion current density was measured according to the linear polarization resistance method (LPRM) [52].

In the LPRM experiments, a stainless steel plate was used as a counter electrode. The steel bar and stainless steel plates were connected to a Potentiostat/Galvanostat. The polarization resistance (R_p) was determined by conducting a linear polarization scan in the range of ±10 mV of the corrosion potential. A scan rate of 0.1 mV/s was used. The corrosion current density (I_{corr}) was determined using the Stern and Geary formula shown below. A schematic representation of the experimental set-up utilized to measure I_{corr} on steel in the concrete specimens is shown in Figure 3-8 while Figure 3-9 shows the actual set-up used in experiment.

$$I_{corr} = B/R_P$$

Where I_{corr} = Corrosion current density, µA/cm^2,

R_p= Polarization resistance, Ω cm^2,

$$B = \frac{(\beta_a * \beta_c)}{2.3(\beta_a + \beta_c)}$$

$\beta_a$and β_c are the anodic and cathodic Tafel constants, mV/decade, respectively.

The Tafel constants are normally obtained by polarizing the steel to 250 mV of the corrosion potential (Tafel plot). However, in the absence of sufficient data on β_a and β_c, a value of B equal to 26 mV for steel in active condition and 52 mV for steel in passive condition is often used.

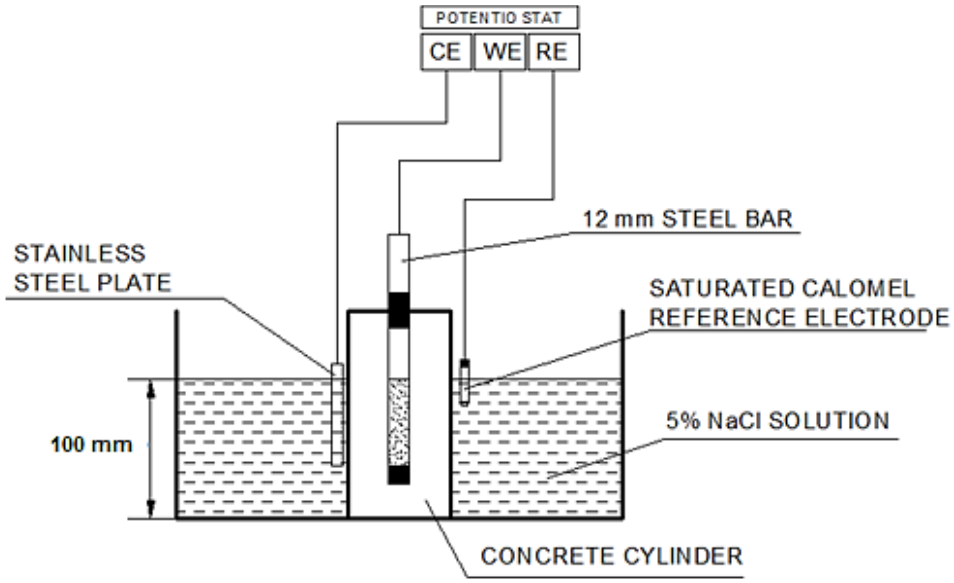

Figure 3-8: Schematic Representation of the Corrosion Current Density set-up

Figure 3-9: Corrosion Current Density Measurement Setup

3.5.7 Sulfate Attack

Ground water and soil contaminated with sulfates (magnesium, sodium and calcium) cause concrete to crack, spall and soften. To assess the performance of all the concrete mixes, specimens, measuring 75 mm in diameter and 150 mm high, were exposed to a solution containing 5% sulfates (2.5% $MgSO_4$, 2.5% Na_2SO_4) after a water curing period of 28 days [53-55]. After 6 and 12 months of exposure to the mixed sulfate environment, the performance of concrete specimens was evaluated through visual examination, weight loss and reduction in compressive strength. Specimens were inspected visually to see the signs of spalling and softening. The compressive strength of the specimens exposed to sulfate salts and specimens of same size which were water cured for the same period were tested. The loss in compressive strength was then calculated by comparing the

compressive strengths of specimens in salt solution with the compressive strength of specimens which were water cured. At the start to exposure the specimens were weighed and the mass was noted after the exposure the specimens were weighed again and the difference of mass was used to calculate the weight loss.

3.5.8 Salt Weathering

Some of the salty water is absorbed, when it comes into contact with concrete either by direct contact or by some other transportation agent but when this contact ends and the concrete starts to dry (low tide time, decrease in ground water table level), the salt present in the pores at the surface expands causing micro-cracks to initiate (Physical damage).

The performance of all the concrete mixes in a salty environment was evaluated by placing 75 mm diameter and 150 mm high concrete specimens in a 15.7% Cl^- plus 0.55% SO_4^{--} (a typical sabkha brine) solution and the specimens where subjected to wet and dry cycles (24 hours wet, 48 hours dry) to simulate the natural wetting and drying of concrete [56-57]. After 6 and 12 months of exposure, the specimens were retrieved and visually examined for surface deterioration and tested to determine the reduction in compressive strength. The compressive strength of the specimens exposed to salt weathering and specimens of same size which were water cured for the same period were tested. The loss in compressive strength was then calculated by comparing the compressive strengths of specimens in salt solution with the compressive strength of specimens which were water cured.

3.5.9 Carbonation

Carbon dioxide present in air, reacts with hydrated cement product [mainly with $Ca(OH)_2$] in the presence of moisture to form $CaCO_3$. This reaction decreases the pH of concrete to 9 and even 8.3 from 13-14. This reduction in pH has detrimental effects on concrete and reinforcement present inside.

Cubic specimens of 50 mm were cast and water cured for a period of 28 days. These mortar specimens were prepared with a water to cement ratio of 0.45 and a sand to cementitious material ratio of 2.75. Thereafter, these specimens were exposed to an accelerated carbonation environment for a period of 90 and 180 days. To distribute CO_2 uniformly, it was passed through 75 mm deep water and specimens were kept 25 mm above the water level. After this period of exposure to the accelerated carbonation environment three mortar specimens representing similar mix properties were split from the middle to show the depth profile with the help of wedge and uni-axial compressive strength machine. Phenolphthalein was sprayed on the freshly-split surfaces. The depth of carbonation was measured according to RILEM Standard CPC 18 [58]. Phenolphthalein gives pink color to indicate the carbonation zone.

CHAPTER 4

RESULTS AND DISCUSSION

The experimental program was discussed in Chapter 3. In this chapter, the results of the experimental work conducted in this study to produce sustainable concrete using the locally available Saudi natural pozzolan and to improve the reactivity of these pozzolans are presented. To improve the reactivity of natural pozzolans, three methods are used. Physically, it was improved by adding silica fume. By adding hydrated lime, it is desired to improve the reactivity chemically. Prolonged grinding of natural pozzolan was carried out to increase its reactivity.

4.1 Compressive Strength

The average compressive strength for all the specimens tested after 7, 14, 28, 90, 180 and 360 days of water curing are listed in Table 4-1. This table presents the compressive strength of the control mix (i.e. 100% OPC used as cementing material) and the other mixes containing natural pozzolan, silica fume and hydrated lime as a partial replacement of OPC.

Table 4-1: Average compressive strength of plain and blended cement concrete

Cementitious Materials	Compressive Strength, MPa					
	Curing Period, Days					
	7	14	28	90	180	360
100% OPC	44.70	52.36	62.73	67.83	71.27	73.48
80% OPC + 20% TYPE 1 NP	36.13	42.60	54.90	60.13	65.93	71.86
80% OPC + 20% TYPE 2 NP	36.90	42.76	52.28	59.33	66.17	72.44
80% OPC + 20% TYPE 3 NP	37.30	41.85	52.93	58.16	64.87	71.04
NP-BLENDED CEMENT 1	38.16	46.90	56.36	64.10	70.33	75.81
NP-BLENDED CEMENT 2	39.43	47.86	56.30	64.65	70.63	76.56
79% OPC + 20% TYPE 1 NP + 1% SF	39.96	45.83	57.73	64.20	69.17	74.12
78% OPC + 20% TYPE 1 NP + 2% SF	40.70	47.63	58.50	65.96	70.27	74.83
77% OPC + 20% TYPE 1 NP + 3% SF	42.06	49.63	60.45	66.83	72.70	76.06
76% OPC + 20% TYPE 1 NP + 4% SF	43.26	51.56	62.33	68.50	73.40	77.31
75% OPC + 20% TYPE 1 NP + 5% SF	43.16	51.40	62.83	65.23	74.00	78.21
79% OPC + 20% TYPE 2 NP + 1% SF	40.26	45.90	56.40	63.20	69.63	74.96
78% OPC + 20% TYPE 2 NP + 2% SF	41.40	47.40	58.16	65.25	70.40	75.12
77% OPC + 20% TYPE 2 NP + 3% SF	43.20	48.36	60.73	66.43	72.40	76.81
76% OPC + 20% TYPE 2 NP + 4% SF	44.60	50.83	63.10	68.86	74.20	77.54
75% OPC + 20% TYPE 2 NP + 5% SF	44.33	51.23	63.55	68.16	73.93	79.12
79% OPC + 20% TYPE 3 NP + 1% SF	40.45	45.65	55.60	60.73	66.80	75.03
78% OPC + 20% TYPE 3 NP + 2% SF	41.06	48.03	58.70	62.20	69.10	76.63
77% OPC + 20% TYPE 3 NP + 3% SF	43.83	49.33	60.35	65.63	71.40	78.15
76% OPC + 20% TYPE 3 NP + 4% SF	44.86	51.83	63.66	68.25	74.03	78.90
75% OPC + 20% TYPE 3 NP + 5% SF	43.73	52.96	63.83	69.30	74.13	79.78
73% OPC + 20% TYPE 1 NP + 7% HL	41.90	50.16	60.10	65.13	72.27	77.30
73% OPC + 20% TYPE 2 NP + 7% HL	40.86	48.43	58.33	64.86	71.83	78.09
73% OPC + 20% TYPE 3 NP + 7% HL	41.16	49.13	57.80	66.16	73.07	78.93
80% OPC + 20% TYPE 1 NP (Fine)	43.90	51.73	61.66	52.43	70.47	74.78
80% OPC + 20% TYPE 2 NP (Fine)	43.60	50.80	59.80	51.40	70.60	75.12
80% OPC + 20% TYPE 3 NP (Fine)	43.85	50.83	60.93	51.87	69.07	75.00

4.1.1 Effect of Natural Pozzolan Addition as a Partial Replacement of OPC on Compressive Strength

Figure 4-1 shows the compressive strength of specimens prepared with partial replacement of OPC with natural pozzolan (20% replacement) along with the control mix. Natural pozzolan from three different sources was used. All the three concrete mixes with natural pozzolan showed lower strength throughout, at all ages. OPC (Control mix) exhibited higher strength. This trend was also reported by Najimi [22], Jamal and Asim [24], Colak [25] and Pekmezci and Akyuz [27]. At early ages, OPC control mix showed higher rate of gain in strength but at later ages the strength of all the four mixes was comparable. After 28 days of water curing, the compressive strength of OPC control mix and Type 1, 2 and 3 NPs, was 62.7, 54.9, 52.3 and 52.9 MPa, respectively. After 360 days of water curing, the compressive strength of the same four mixes was 73.5, 71.9, 72.4 and 71.0 MPa, respectively, which are comparable.

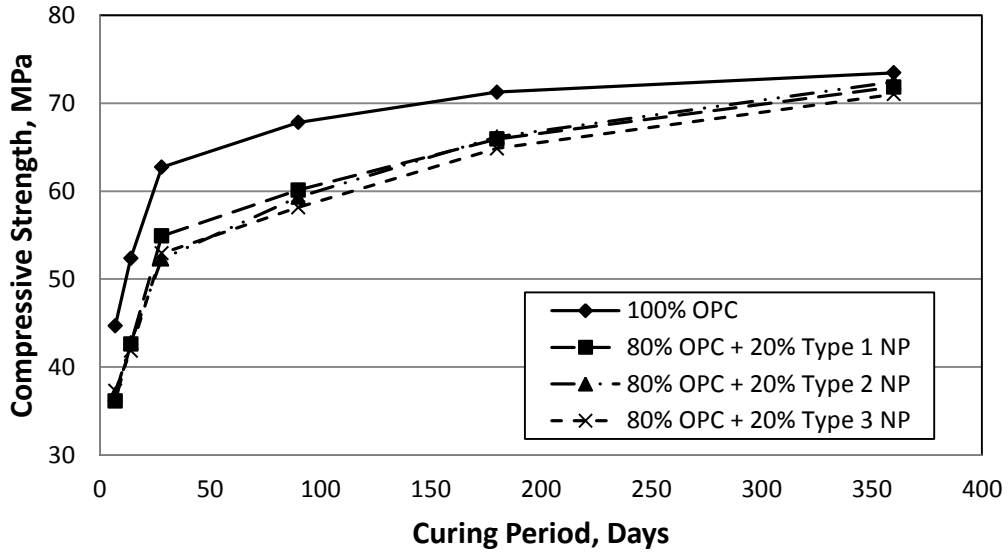

Figure 4-1: Compressive strength development of 20% NP and control mixes.

4.1.2 Effect of Physical Activation of Natural Pozzolan on Compressive Strength

The compressive strength developed over an age of 360 days by concrete specimens prepared with a constant 20% dosage of Type 1, 2 and 3 NPs and varying SF content (1 to 5%) is shown in Figures 4-2, 4-3 and 4-4, respectively. It is clearly seen that with an increase in the SF content there is an improvement in compressive strength for all the types of NPs. The least improvement is seen when 1% SF was added. The highest improvement in the compressive strength was noted when 5% SF was added to the mix. This trend was seen at all ages. After 360 days of water curing, the highest compressive strength recorded of 79.8 MPa was noted in concrete with 20% Type 3 NP and 5% SF, as a partial replacement of OPC. The least strength of 74.1 MPa was noted in 20% Type 1 NP and 1% SF, as a partial replacement of OPC.

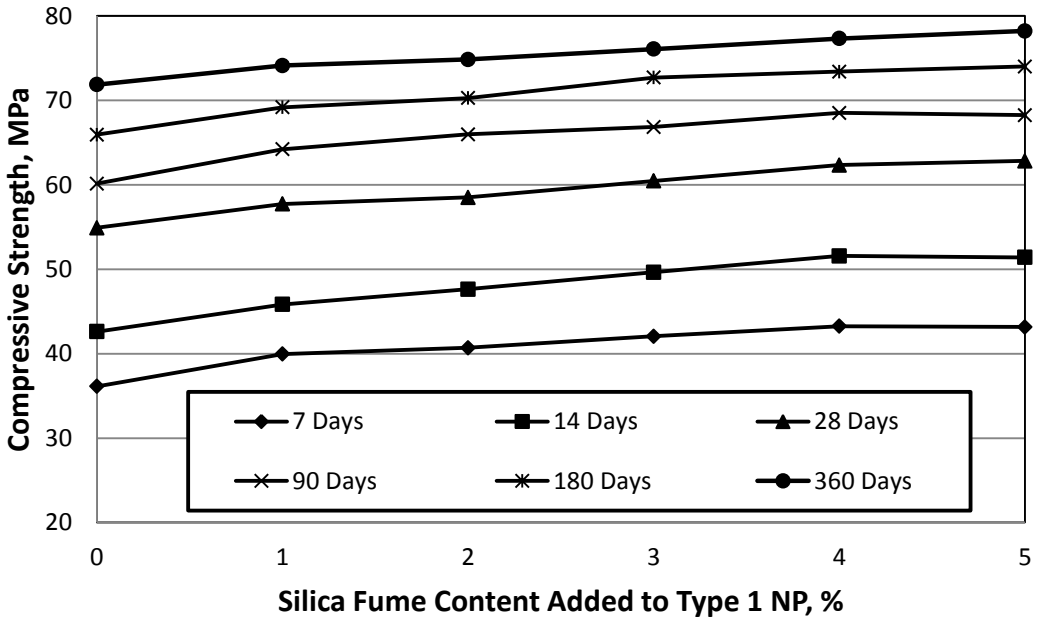

Figure 4-2: Compressive strength development of Type 1 NP plus SF

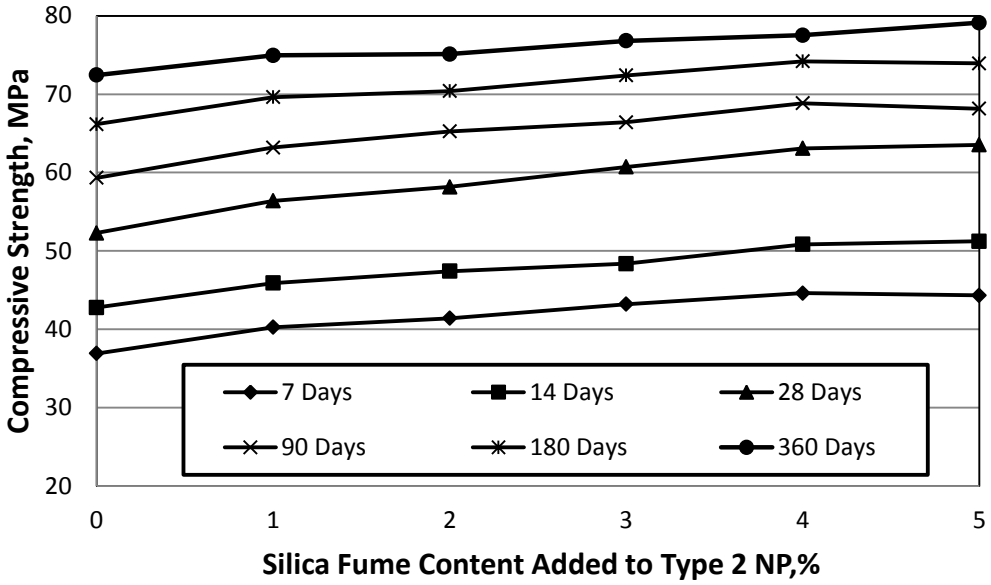

Figure 4-3: Compressive strength development of Type 2 NP plus SF

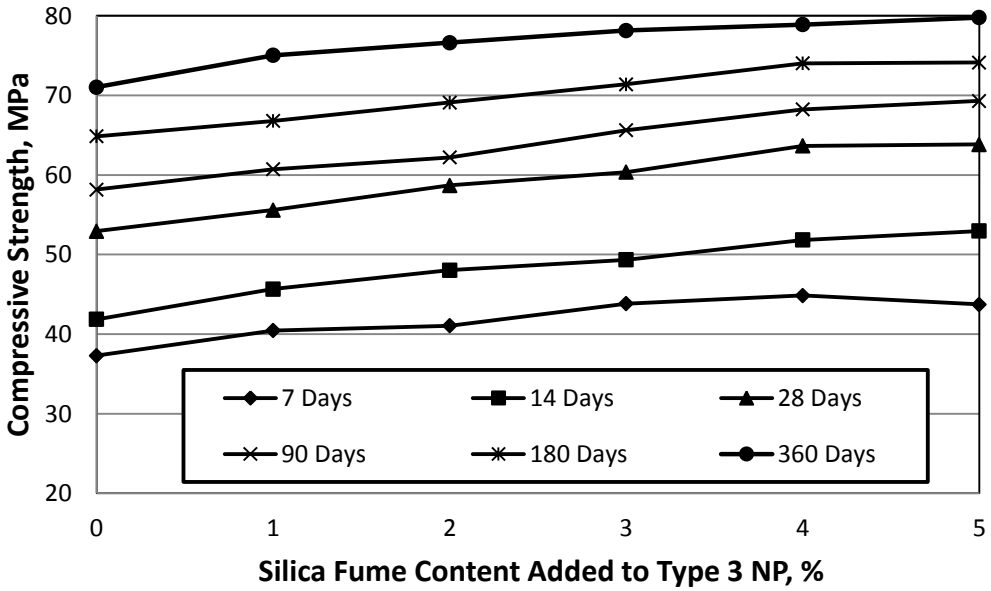

Figure 4-4: Compressive strength development of Type 3 NP plus SF

By analyzing the data in Figures 4-2, 4-3 and 4-4, it is apparent that the least improvement in compressive strength is noted when 1% SF is added and the highest improvement in compressive strength was noted in the specimens with 5% SF. Figures 4-5, 4-6 and 4-7 show the compressive strength with SF. In all the three cases of Type 1, 2 and 3 NP, by adding SF, a clear improvement in compressive strength of specimens which were prepared without SF and only 20% NP could be noted. Also, the compressive strength of the specimens prepared with 1% SF and 20% NP is comparable with that of the OPC control specimens after 360 days of water curing for all three types of NP. The addition of 5% SF to 20% NP showed good improvement. After 28 days of water curing, the compressive strength of specimens with 5% SF and 20% NP is comparable to strength of OPC specimens for all three types of NP. After the 360 days of curing, these specimens showed higher compressive strength than that of OPC specimens. It was reported by Poon et al. [32] that the addition of 5 and 10% SF, as a partial replacement of OPC, showed lower strength then control OPC mix, till 28 days; thereafter, the mixes with SF showed higher strength than OPC. Bhanja and Sengupta [33] reported that at 28 days, the strength of all mixes containing SF, as a partial replacement of OPC, showed higher strength than the OPC control mix.

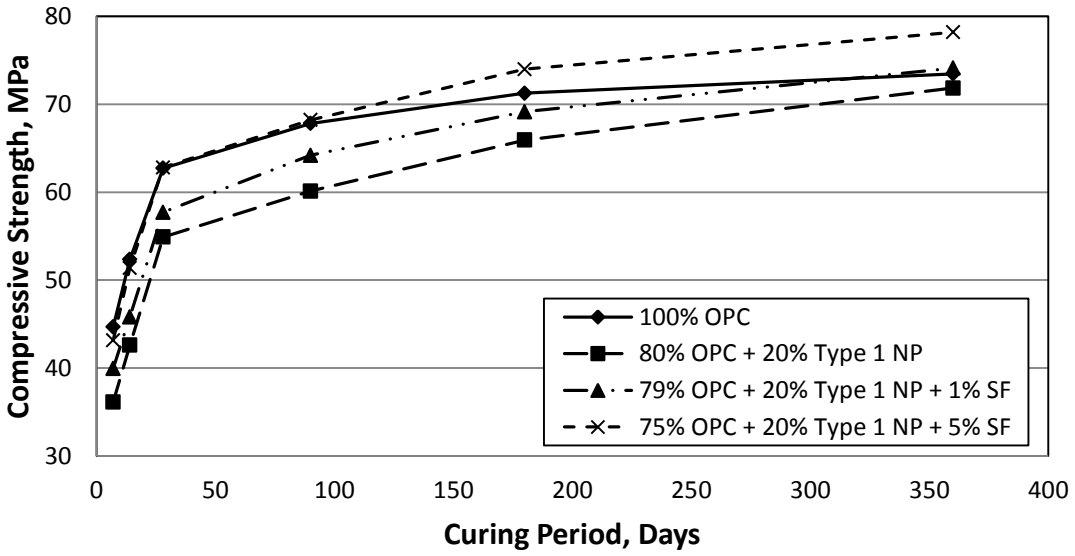

Figure 4-5: Compressive strength development of specimens with SF and Type 1 NP

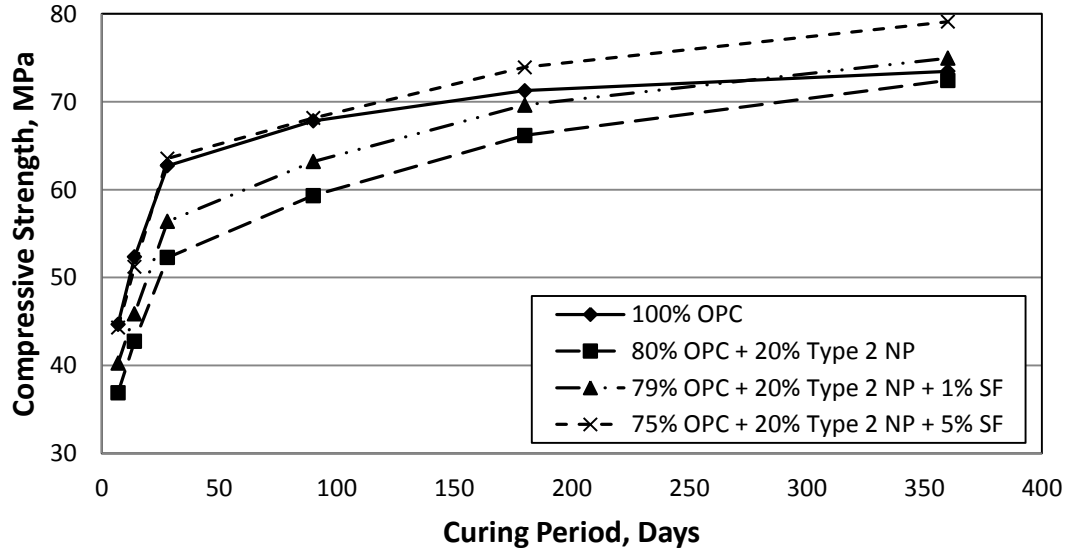

Figure 4-6: Compressive strength development of specimens with SF and Type 2 NP

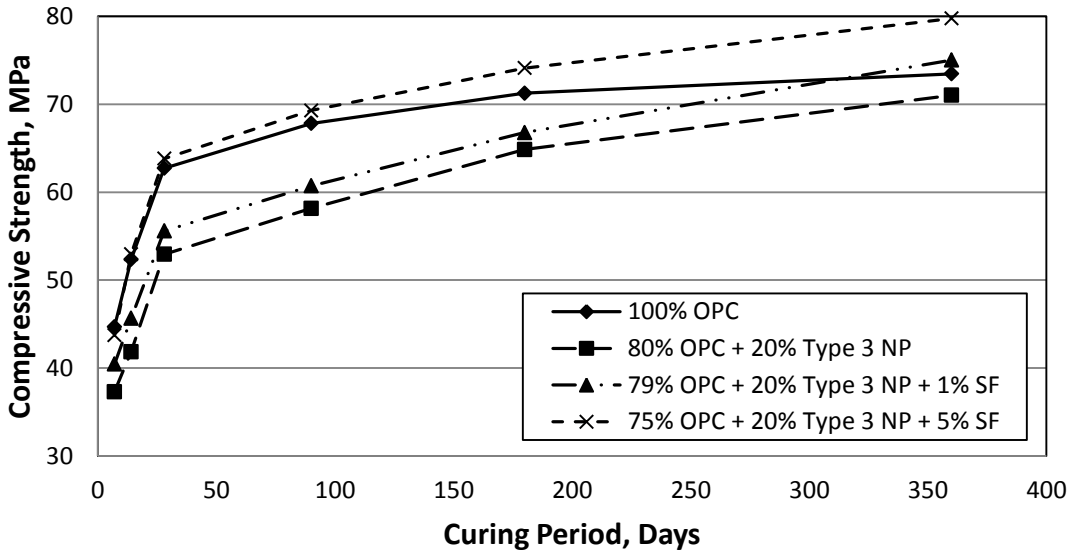

Figure 4-7: Compressive strength development of specimens with SF and Type 3 NP

4.1.3 Effect of Chemical Activation of Natural Pozzolan on Compressive Strength

The compressive strength development of specimens prepared with the addition of 7% HL to all three types of NP, as a scheme to improve the reactivity of NP chemically, is shown in Figures 4-8 through 4-10. HL clearly worked as a chemical activating agent and improved the compressive strength of NP concrete. At early ages, the rate of strength development for specimens with HL is higher than the specimens without HL. This trend is true for all the three Types of NP. After 180 days of water curing, the compressive strength of specimens with Type 1 and 2 NP is comparable with OPC, while the specimen of Type 3 NP with HL shows higher strength than the control specimens. At 360 days of water curing, all the specimens of three types of NPs with HL showed higher

strength than OPC control specimens. After 360 days of Water curing, the compressive strength of Type 1, 2 and 3 with HL are 77.3, 78.1 and 78.9 respectively, as compared with 73.4 MPa for the control specimens. Shi and Day [27] used hydrated lime with NP and used chemical reagents like sodium sulfate and calcium chloride as chemical activators and reported an increase in the strength due to the addition of hydrated lime. Ghrici [16] reported that at 28 days, the strength for all the mixes with limestone powder and NP was less than OPC but at 90 days, the mix with 20% NP and 10% limestone powder showed higher strength than OPC control mix. The additional strength at later period of curing is a result of the secondary hydration products formed due to the reaction of HL with NPs. This pozzolanic reaction replaces lime with C-S-H in the concrete which translates into higher strength than that of OPC.

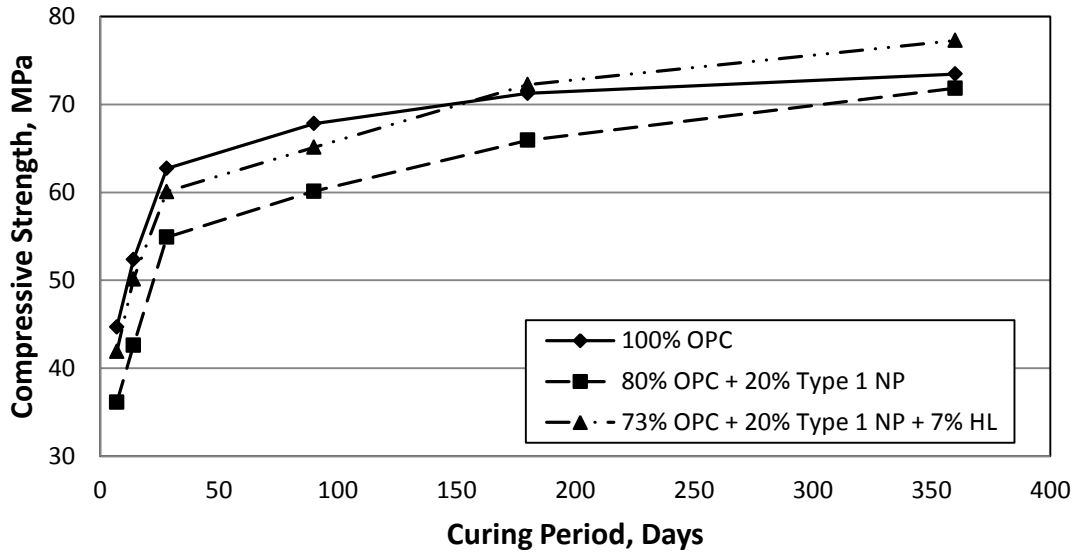

Figure 4-8: Compressive strength development of specimens with HL and Type 1 NP

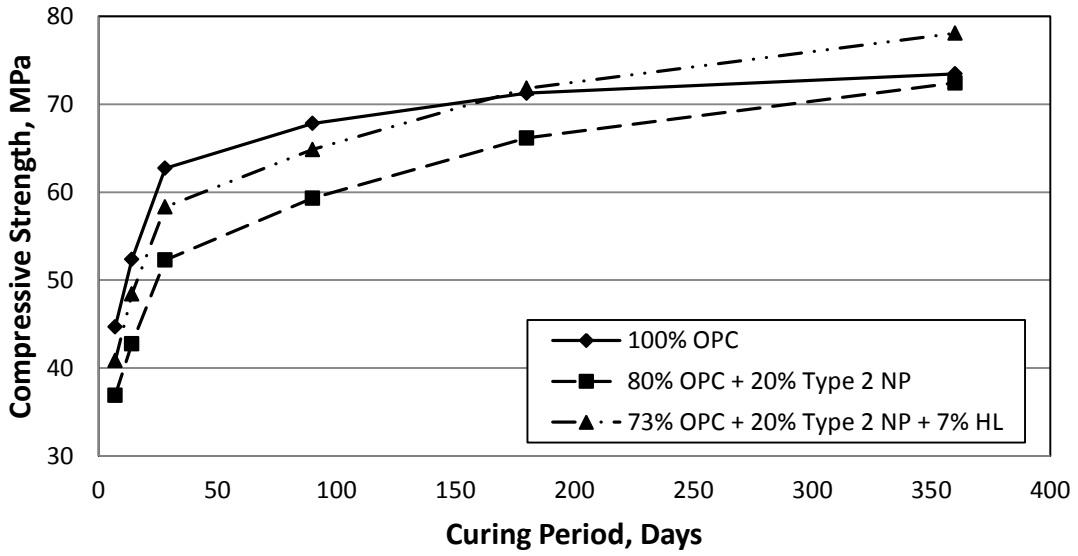

Figure 4-9: Compressive strength development of specimens with HL and Type 2 NP

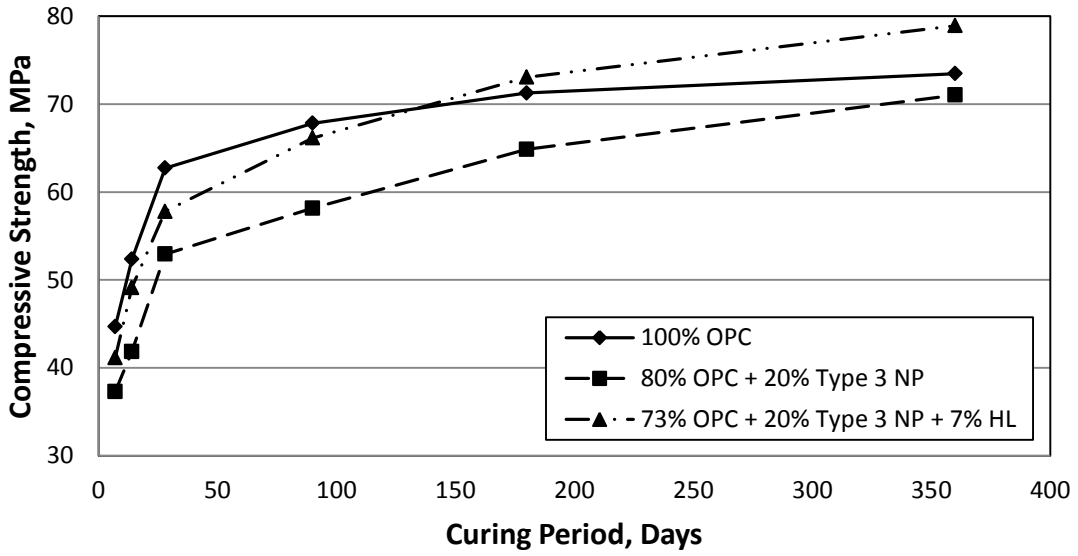

Figure 4-10: Compressive strength development of specimens with HL and Type 3 NP

4.1.4 Effects of Mechanical Activation of Natural Pozzolan on Compressive Strength

All the three types of NP were grinded for prolonged period to get finer pozzolanic material (i.e. larger surface area) and then used in the same quantity as their coarser counterparts as a partial replacement of OPC, i.e. 20%. Figures 4-11 through 4-13 show the compressive strength development of finer Type 1, 2 and 3 NP, respectively. The three types of fine NP showed higher rate of strength gain at the initial period of curing thereby signifying that the rate of hydration was higher than the coarser NP of same type. Day and Shi [26] reported that the effect of fineness was most profound at early ages. After 360 days of water curing, the compressive strength was comparable for both the fine and coarse NP. Shi and Day [27] reported an increase in the strength due to an increase of fineness but this increase was not significant at 28 days. An increase in the fineness from 291 m^2/kg to 385 m^2/kg increased the compressive strength by only11%.

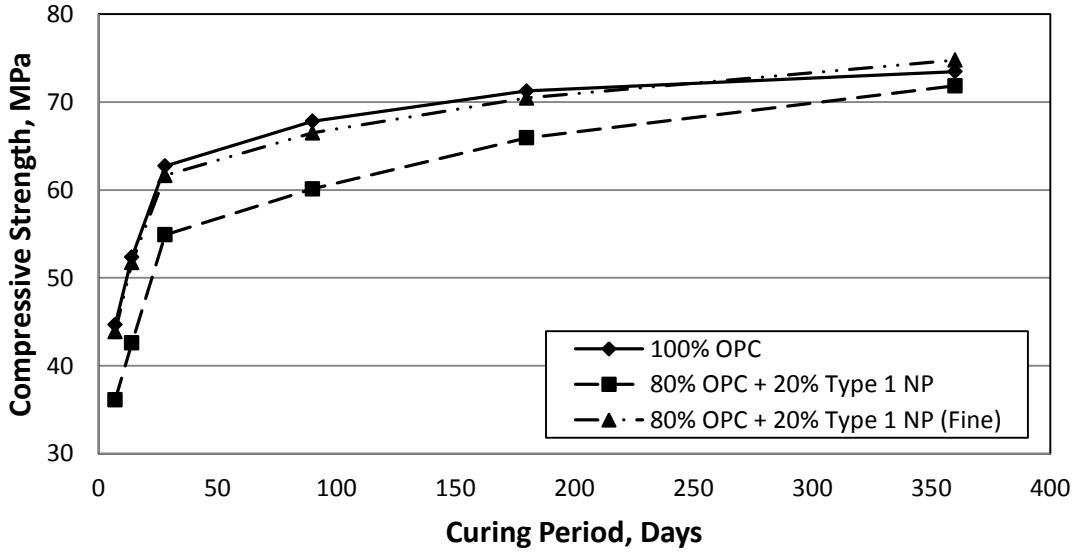

Figure 4-11: Compressive strength development of specimens of finer Type 1 NP

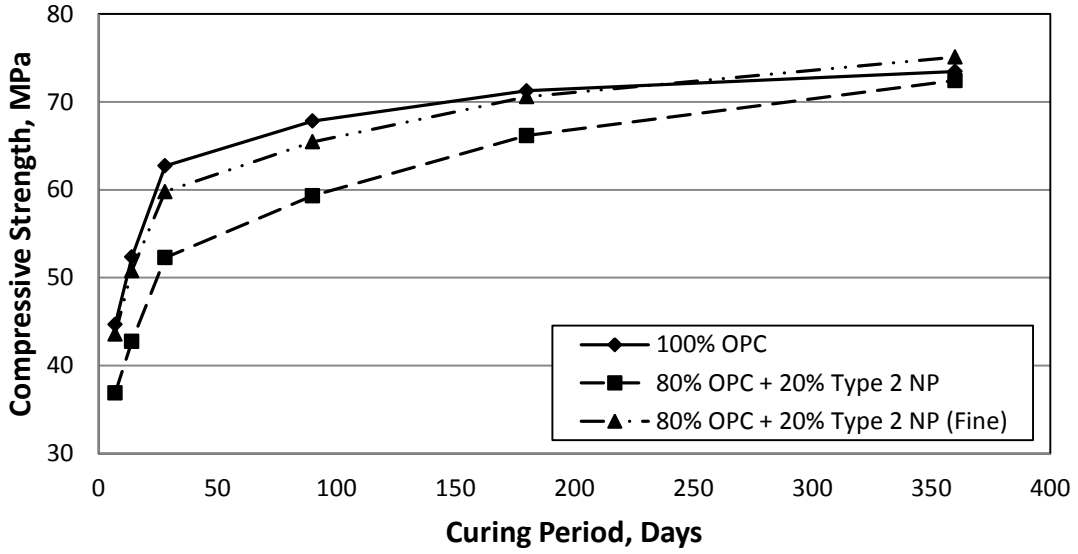

Figure 4-12: Compressive strength development of specimens of finer Type 2 NP

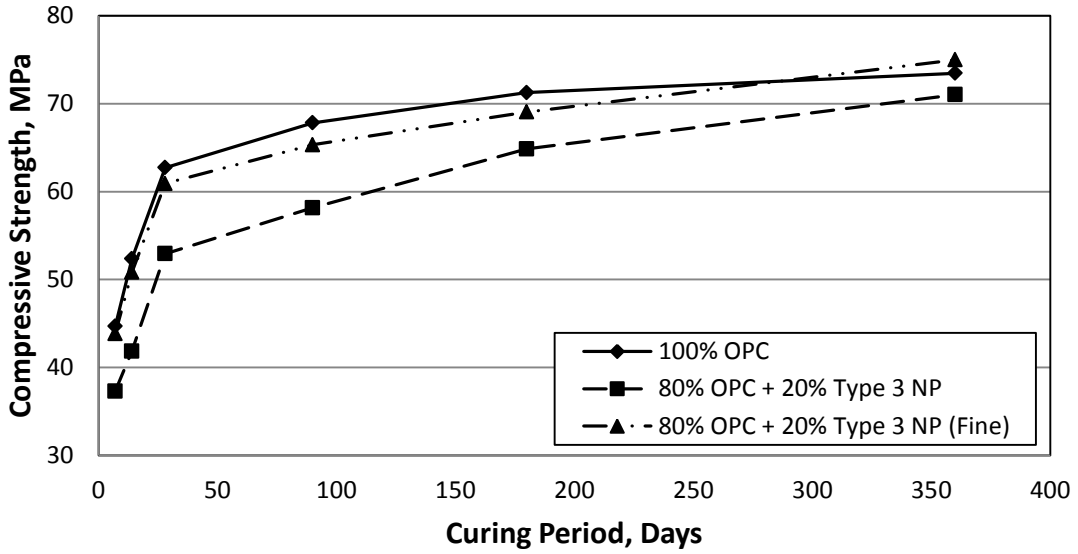

Figure 4-13: Compressive strength development of specimens of finer Type 3 NP

4.1.5 Compressive Strength of Blended Cements

The compressive strength development of specimens prepared with two blended cements obtained from local cement factories is shown in Figure 4-14. Both the cements showed almost identical compressive strengths at all curing periods. After 180 days of water curing, the strength of both the blended cements were comparable to OPC, while the strength for both the blended cements was higher than OPC after 360 days of water curing. It is seen in the discussions above that the natural pozzolans used in this study are not very reactive at early periods of curing; it is the later part of the curing where they started to show some pozzolanic reactivity that is reflected by the higher strengths of NP concretes that is comparable to OPC concrete at 360 days as can be seen in Figure 4-1.

Since the performance of these three natural pozzolans are almost similar and these NP-blended cements were also produced from similar pozzolans that is locally available in Saudi Arabia, therefore, the performance of NP-blended cement concretes would be more or less similar to that of concrete prepared with all three types of NPs. This could be the reason why the strengths of both the NP-blended cement concretes was less than that of OPC concrete at early periods of curing. However, after an extended period of curing the strengths of these NP-blended cement concretes was relatively higher than that of the OPC concrete.

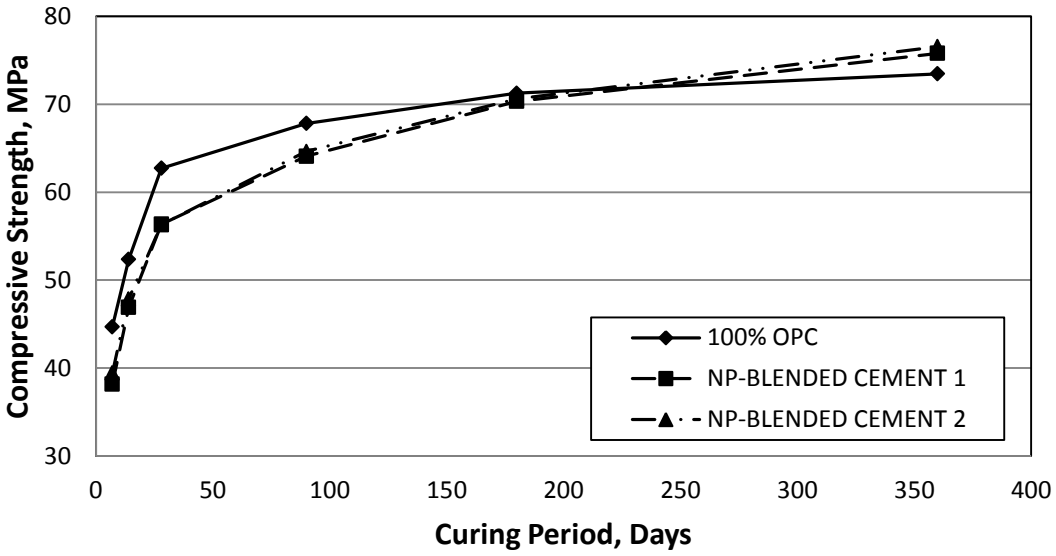

Figure 4-14: Compressive strength development of specimens prepared with NP-blended cements

4.2 Depth of Water Penetration

Table 4-2 summarizes the average values of depth of water penetration for all the specimens. Further, Table 4-3 shows the classification, based on the criteria for water penetration depth, as presented in Table 3-9. After 28 days of water curing, almost all the specimens showed low water penetration with some specimens in the moderate depth of penetration range. After 90 and 180 days of water curing, all specimens showed low depth of penetration. Table 4-2 also shows that the water penetration depth in NP concrete specimens were less than that of OPC specimens, even at 28 days; signifying that the addition of NP was improving the micro-structure of concrete (i.e. making it denser and more impermeable). The difference of depth of water penetration in NP and OPC concretes increased at later curing periods (i.e. 90 and 180 days), reflecting the late pozzolanic reaction of these pozzolans.

Table 4-2: Average depth of water penetration

Cementitious Materials	Depth of Water Penetration (mm)		
	Curing Period, Days		
	28	90	180
100% OPC	35.3	30.3	29.3
80% OPC + 20% Type 1 NP	29.7	21.7	18.7
80% OPC + 20% Type 2 NP	31.7	23.3	21.0
80% OPC + 20% Type 3 NP	32.0	24.0	20.7
NP-BLENDED CEMENT 1	27.7	19.3	15.7
NP-BLENDED CEMENT 2	26.3	16.7	14.0
79% OPC + 20% Type 1 NP + 1% SF	29.3	20.3	16.7
78% OPC + 20% Type 1 NP + 2% SF	26.7	19.0	16.0
77% OPC + 20% Type 1 NP + 3% SF	25.3	20.7	16.7
76% OPC + 20% Type 1 NP + 4% SF	22.0	15.3	12.3
75% OPC + 20% Type 1 NP + 5% SF	21.7	14.0	11.0
79% OPC + 20% Type 2 NP + 1% SF	32.7	23.7	20.7
78% OPC + 20% Type 2 NP + 2% SF	24.0	21.3	18.3
77% OPC + 20% Type 2 NP + 3% SF	23.7	17.7	15.3
76% OPC + 20% Type 2 NP + 4% SF	22.7	14.7	11.7
75% OPC + 20% Type 2 NP + 5% SF	18.0	12.0	8.7
79% OPC + 20% Type 3 NP + 1% SF	29.3	23.0	20.0
78% OPC + 20% Type 3 NP + 2% SF	27.3	21.0	19.7
77% OPC + 20% Type 3 NP + 3% SF	23.7	16.0	12.3
76% OPC + 20% Type 3 NP + 4% SF	14.7	13.3	10.3
75% OPC + 20% Type 3 NP + 5% SF	15.0	10.3	6.7
73% OPC + 20% Type 1 NP + 7% HL	27.3	18.7	15.3
73% OPC + 20% Type 2 NP + 7% HL	28.3	20.0	17.7
73% OPC + 20% Type 3 NP + 7% HL	25.3	16.7	14.3
80% OPC + 20% Type 1 NP (Fine)	25.3	18.7	13.7
80% OPC + 20% Type 2 NP (Fine)	25.7	20.0	17.3
80% OPC + 20% Type 3 NP (Fine)	28.0	19.3	15.3

Table 4-3: Classification of concrete based on depth of water penetration

Cementitious Materials	Depth of Water Penetration (mm)		
	Curing Period, Days		
	28	90	180
100% OPC	35.3 (M)	30.3(M)	29.3(L)
80% OPC + 20% Type 1 NP	29.7(L)	21.7(L)	18.7(L)
80% OPC + 20% Type 2 NP	31.7(M)	23.3(L)	21.0(L)
80% OPC + 20% Type 3 NP	32.0(M)	24.0(L)	20.7(L)
NP-BLENDED CEMENT 1	27.7(L)	19.3(L)	15.7(L)
NP-BLENDED CEMENT 2	26.3(L)	16.7(L)	14.0(L)
79% OPC + 20% Type 1 NP + 1% SF	29.3(L)	20.3(L)	16.7(L)
78% OPC + 20% Type 1 NP + 2% SF	26.7(L)	19.0(L)	16.0(L)
77% OPC + 20% Type 1 NP + 3% SF	25.3(L)	20.7(L)	16.7(L)
76% OPC + 20% Type 1 NP + 4% SF	22.0(L)	15.3(L)	12.3(L)
75% OPC + 20% Type 1 NP + 5% SF	21.7(L)	14.0(L)	11.0(L)
79% OPC + 20% Type 2 NP + 1% SF	32.7(M)	23.7(L)	20.7(L)
78% OPC + 20% Type 2 NP + 2% SF	24.0(L)	21.3(L)	18.3(L)
77% OPC + 20% Type 2 NP + 3% SF	23.7(L)	17.7(L)	15.3(L)
76% OPC + 20% Type 2 NP + 4% SF	22.7(L)	14.7(L)	11.7(L)
75% OPC + 20% Type 2 NP + 5% SF	18.0(L)	12.0(L)	8.7(L)
79% OPC + 20% Type 3 NP + 1% SF	29.3(L)	23.0(L)	20.0(L)
78% OPC + 20% Type 3 NP + 2% SF	27.3(L)	21.0(L)	19.7(L)
77% OPC + 20% Type 3 NP + 3% SF	23.7(L)	16.0(L)	12.3(L)
76% OPC + 20% Type 3 NP + 4% SF	14.7(L)	13.3(L)	10.3(L)
75% OPC + 20% Type 3 NP + 5% SF	15.0(L)	10.3(L)	6.7(L)
73% OPC + 20% Type 1 NP + 7% HL	27.3(L)	18.7(L)	15.3(L)
73% OPC + 20% Type 2 NP + 7% HL	28.3(L)	20.0(L)	17.7(L)
73% OPC + 20% Type 3 NP + 7% HL	25.3(L)	16.7(L)	14.3(L)
80% OPC + 20% Type 1 NP (Fine)	25.3(L)	18.7(L)	13.7(L)
80% OPC + 20% Type 2 NP (Fine)	25.7(L)	20.0(L)	17.3(L)
80% OPC + 20% Type 3 NP (Fine)	28.0(L)	19.3(L)	15.3(L)

4.2.1 Effects of Natural Pozzolan Addition as a Partial Replacement of OPC on the Depth of Water Penetration

Figure 4-15 shows the variation of the depth of water penetration specimens; OPC and all three types of NP specimens. The specimens prepared with partial replacement of OPC with NP exhibited lower depth of water penetration. Najimi et al. [19] reported that, replacing OPC with 15 and 30% NP decreased the depth of water penetration after 28 and 90 days of water curing. This is true for all curing periods at which the test was conducted, but the difference is more obvious at later ages (i.e. 180 days). This is may be due to the fact that NP takes some time to react and at later stage it helps in refining the pore structure making the mirco-structure denser which results in low water penetration. This is also reflected by higher compressive strengths of NP concretes at later curing periods which are comparable to that of OPC, as shown in Figure 4-1. After 180 days of water curing, replacement of 20% OPC with NP helped decrease the depth of water penetration from 29.3 mm in OPC concrete to 18.7, 21.0 and 20.7 mm in Type 1, 2 and 3 NP concretes, respectively. This accounts for a reduction in water penetration depth by 36, 28 and 29%, respectively.

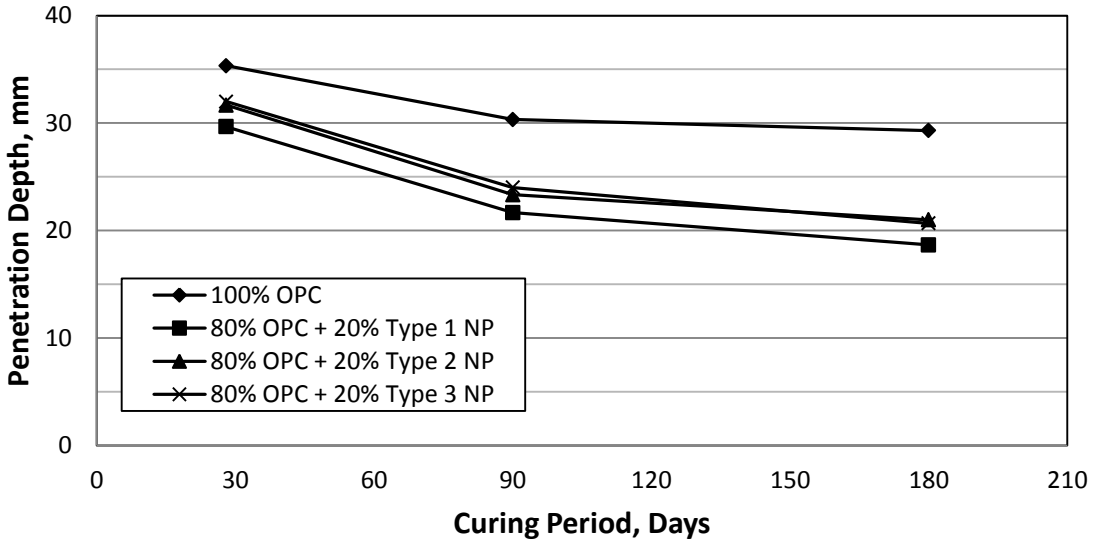

Figure 4-15: Depth of water penetration in OPC and three types of NP.

4.2.2 Effect of Physical Activation of Natural Pozzolan on the Depth of Water Penetration

The addition of SF for physical activation of natural pozzolan has clearly worked to decrease the water penetration depth. Figure 4-16 through 4-18 show the depth of water penetration of specimens prepared by adding 1 to 5% SF to 20% Type 1, 2 and 3 NP, respectively. It is clearly seen that in all the three cases as the dosage of SF was increased, the depth of penetration decreased. At 28 days, the highest penetration depth was recorded in the specimens prepared with 1% SF and 20% Type 2 NP, which is 32.7 mm. The lowest penetration recorded was in specimen prepared with 5% SF and 20% NP, Type 3 which is 15.0 mm.

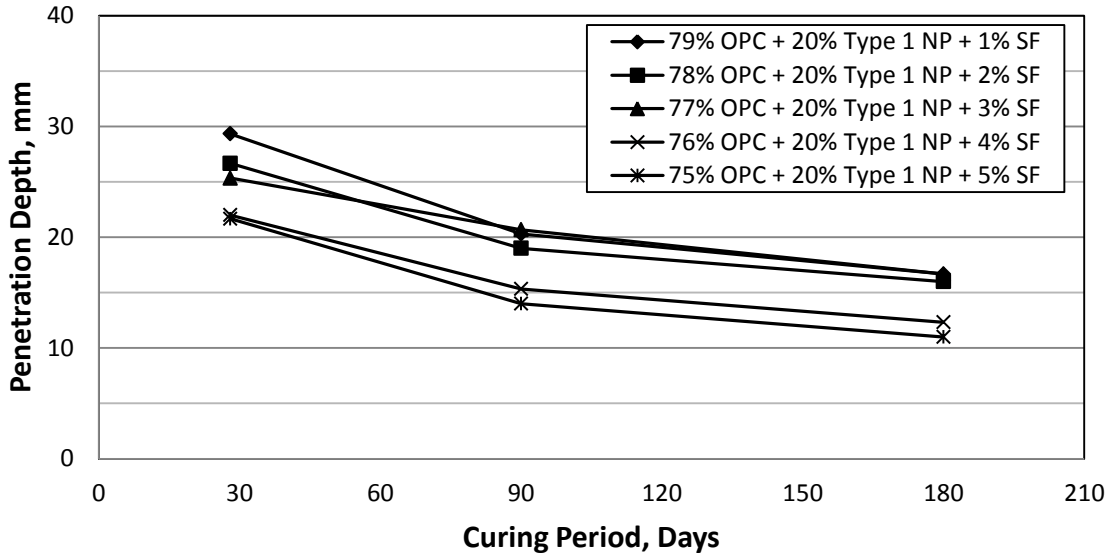

Figure 4-16: Depth of water penetration for specimens with varying SF content and 20% Type 1 NP

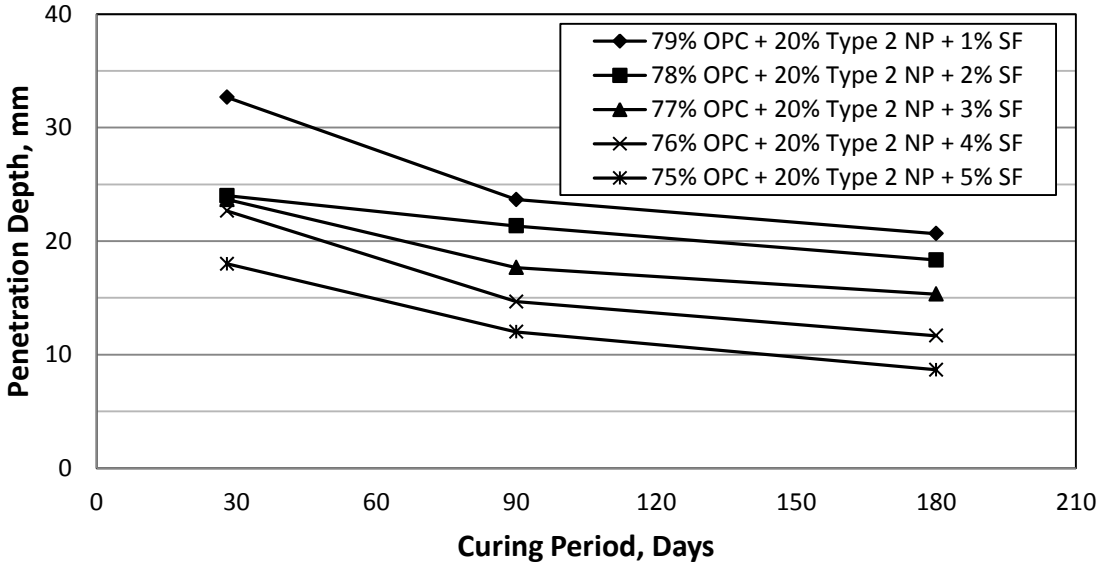

Figure 4-17: Depth of water penetration for specimens with varying SF content and 20% Type 2 NP

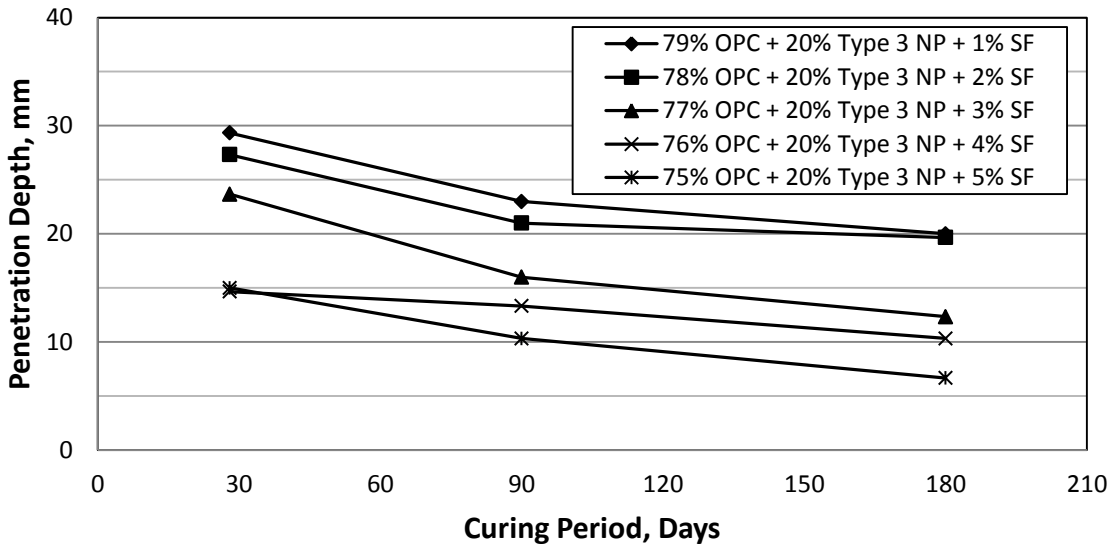

Figure 4-18: Depth of water penetration for specimens with varying SF content and 20% Type 3 NP

It is seen from the above figures that the least water penetration depth is observed in the specimens prepared with 5% SF and the maximum in the specimens prepared with 1% SF. Figures 4-19, 4-20 and 4-21 show the comparison of these specimens of Type 1, 2 and 3 NPs respectively, with OPC concrete specimens. The addition of NP decreased the water penetration depth as compared with OPC concrete. With the inclusion of SF, the performance of specimens was enhanced. Silica fume is a super-pozzolanic material that is known for its early pozzolanic reaction. It refines the pore structure making concrete more dense [31-33]. After 180 days of curing, the depth of water penetration of the specimens prepared with the addition of 1% SF was 16.7, 20.7 and 20.0 mm for all three types of NP concretes, compared to 29.3 mm in OPC concrete specimens. It was 29 to 43% less than that of OPC specimens. The depth of water penetration of specimens with 5% SF was 11.0, 8.7 and 6.7 mm for all three types of NP concretes which was 62 to 77% less than that of OPC specimens. Studies show that the depth of water penetration

for concrete specimens decrease with the addition of SF, compared to specimens of OPC concrete [59-61].

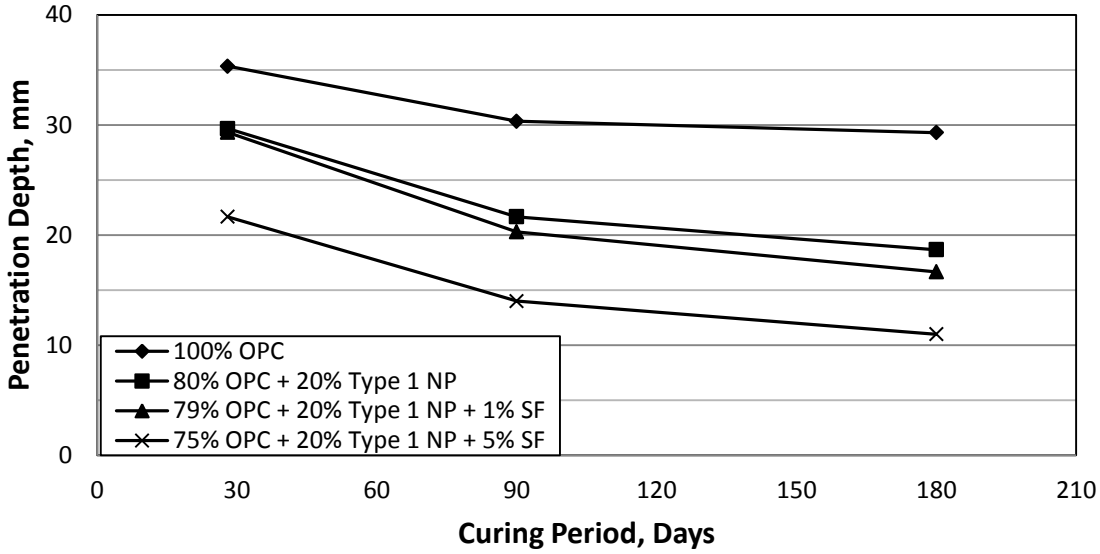

Figure 4-19: Comparison of the depth of water penetration of OPC with SF and Type 1 NP

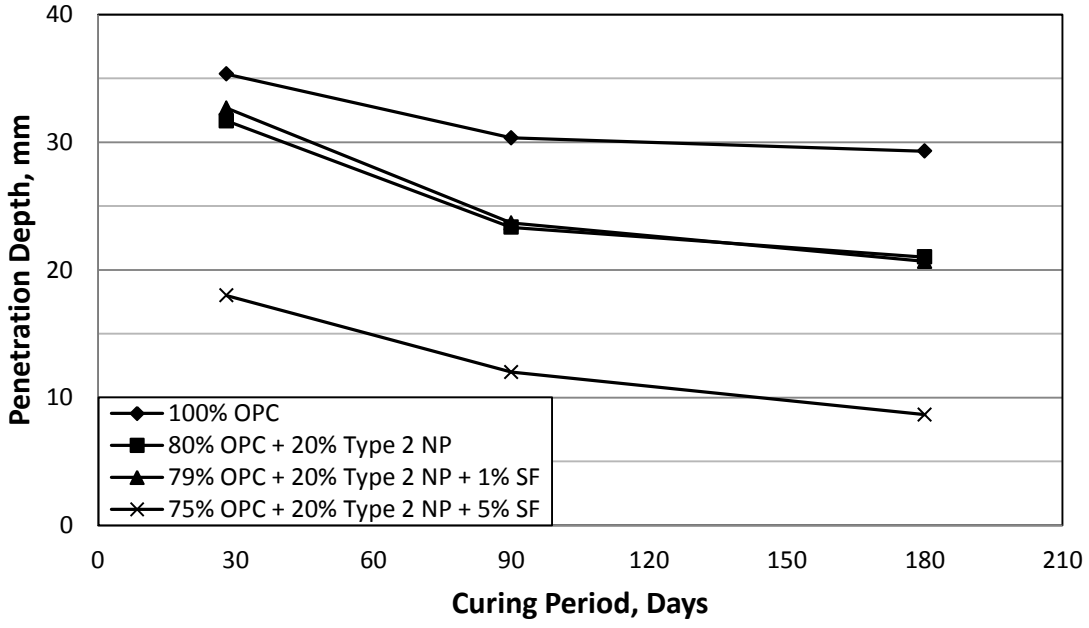

Figure 4-20: Comparison of the depth of water penetration of OPC with SF and Type 2 NP

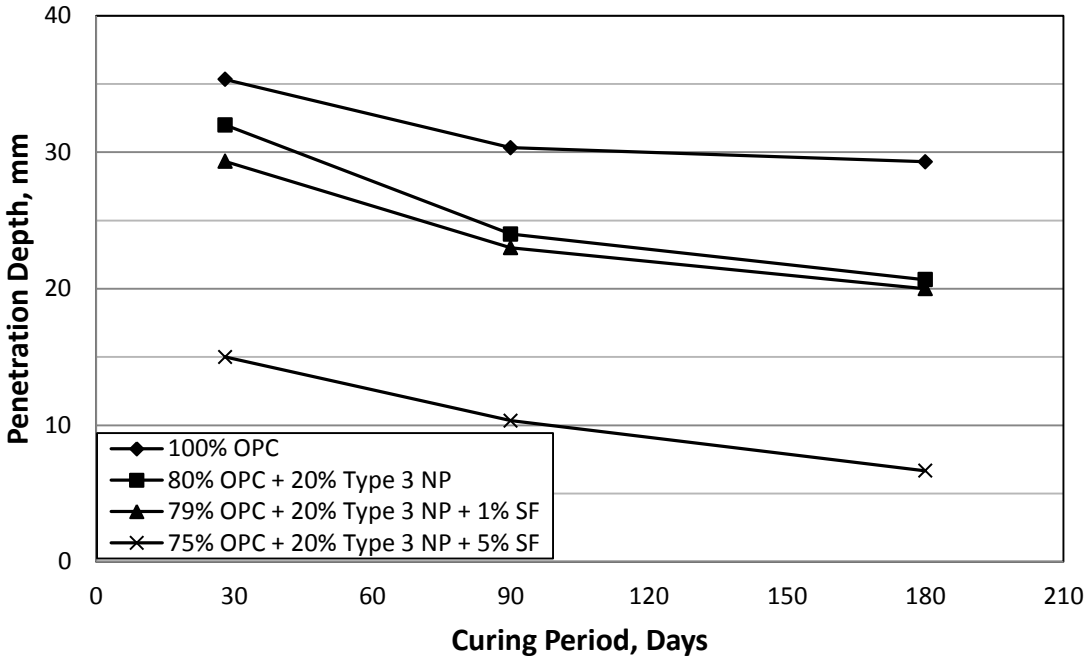

Figure 4-21: Comparison of the depth of water penetration of OPC with SF and Type 3 NP

4.2.3 Effects of Chemical Activation of Natural Pozzolan on the Depth of Water Penetration

Figures 4-22 through 4-24 show the comparison of the depth of water penetration in OPC, 20% NP and NP activated with HL. In all three types of NP, the addition of HL helped decreasing the depth of water penetration. This improvement was not as significant as it was when SF was added to NP specimens. Zelic et al. [29] studied the ternary mixes of OPC-lime-SF and reported that adding lime to OPC-SF increased the porosity of mortars. This porosity was higher than that of OPC control mix; however the pores were not connected and the permeability was not affected. In fact, addition of HL decreased the depth of water penetration of concrete. Addition of HL to Type 3 NP

exhibited more improvement than in the other two types of NP. After 180 days of water curing, the depth of water penetration in specimens prepared with the addition of HL to all three types of NPs was 15.3, 17.7 and 14.3 mm, compared to 29.3 mm in OPC.

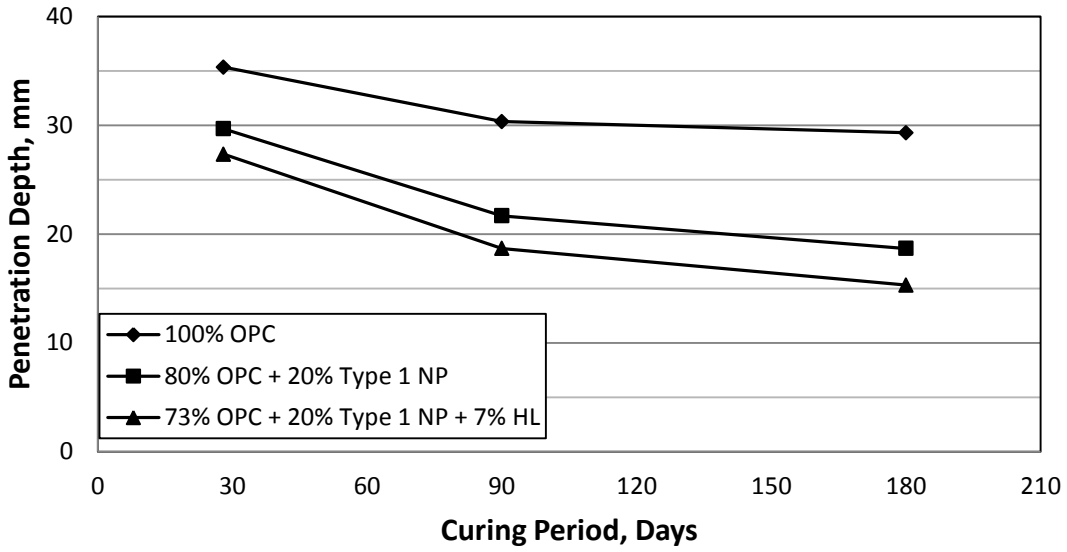

Figure 4-22: Depth of Water penetration of specimens with HL and Type 1 NP

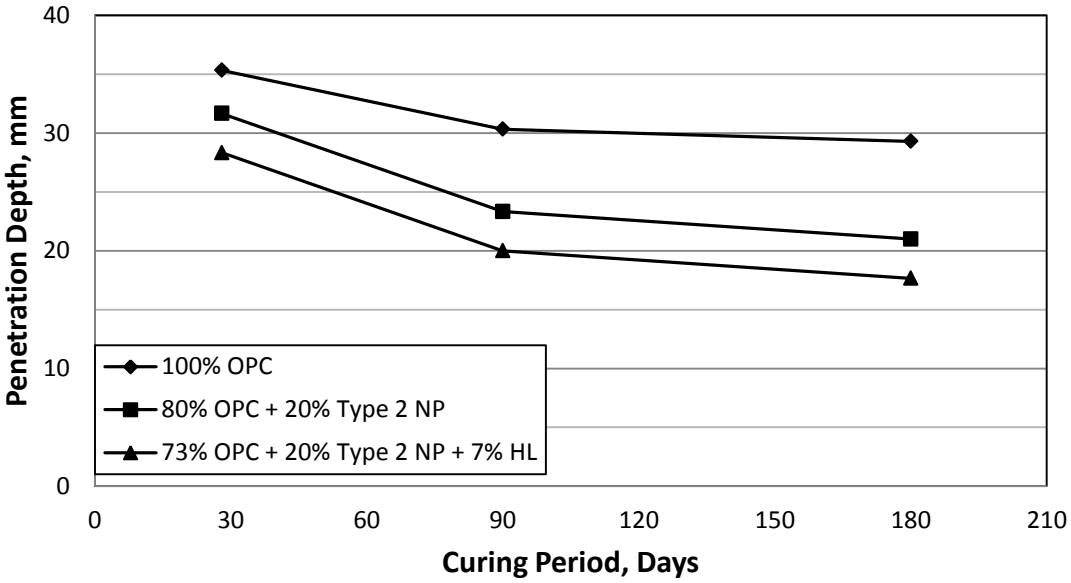

Figure 4-23: Depth of Water penetration of specimens with HL and Type 2 NP

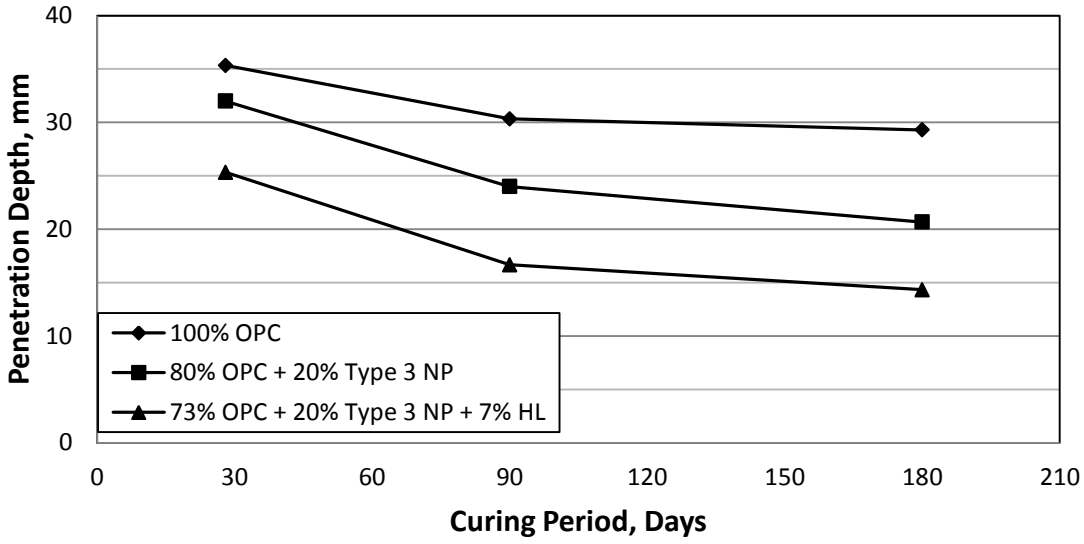

Figure 4-24: Depth of Water penetration of specimens with HL and Type 3 NP

4.2.4 Effects of Mechanical Activation of Natural Pozzolan on Depth of Water Penetration

Figures 4-25 through 4-27 show the depth of water penetration in specimens prepared with 20% NP as a partial replacement of cement and OPC specimens. NP with two finenesses was used to prepare two different specimens. In all three types of NP, increasing the fineness helped decrease the water penetration. The water penetration depth of coarse Type 1 NP, after 180 days of water curing, was 18.7 mm, while it was 13.7 mm for finer Type 1 NP. This showed that increasing the fineness of NP decreased the depth of water penetration of Type 1 NP concrete by 26%. For Type 2 and 3 NPs the decrease in the depth of water penetration of NP concretes was 17 and 26%, respectively, as the fineness of NP was increased. Fine NP, compared to coarse NP, has larger surface

area and it is slightly more reactive and has more packing ability making concrete denser, which is why the depth of water penetration decreased for all the three types of NP.

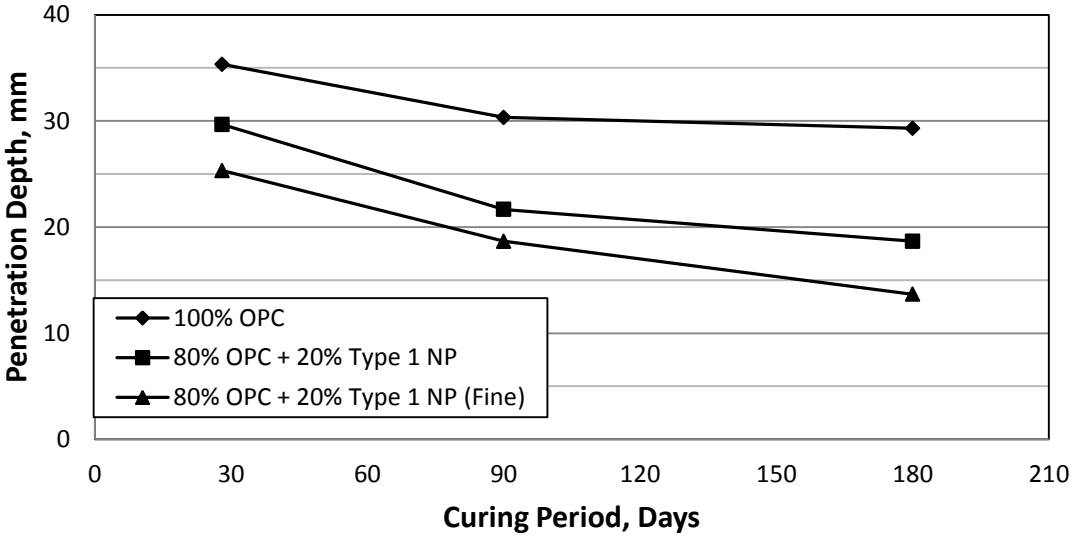

Figure 4-25: Depth of water penetration in specimens of finer Type 1 NP

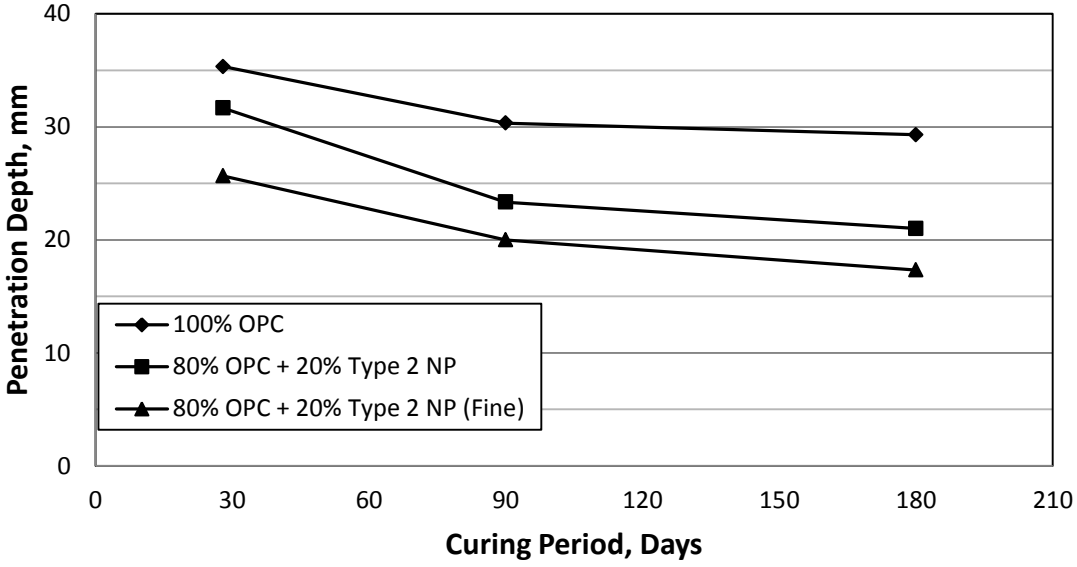

Figure 4-26: Depth of water penetration in specimens of finer Type 2 NP

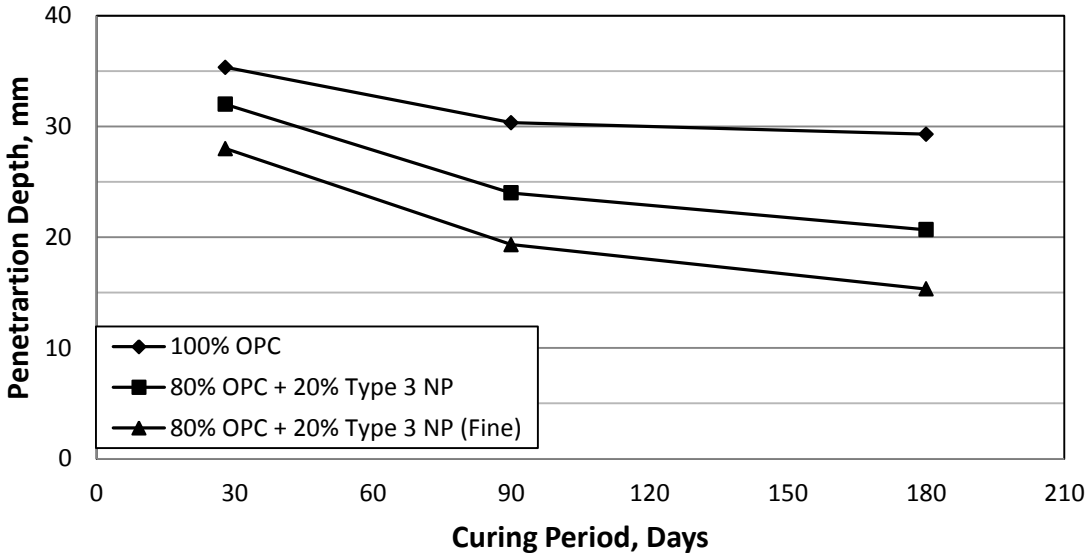

Figure 4-27: Depth of water penetration in specimens of finer Type 3 NP

4.2.5 Depth of Water Penetration in Blended Cements

Figure 4-28 shows the depth of water penetration in the specimens prepared with two NP-blended cements in comparison with OPC concrete. Both the NP-blended cements showed significant improvement and the depth of water penetration in NP-blended cement concretes were less than that of OPC specimens. After 180 days of water curing, the depth of water penetration in both the NP-blended cement concretes was 15.7 and 14.0 mm, compared to 29.3 mm in OPC specimens. As discussed in Section 4.2.1, the use of natural pozzolan in concrete reduces the depth of water penetration. Similarly, the NP-blended cement concretes also provide with the same advantage.

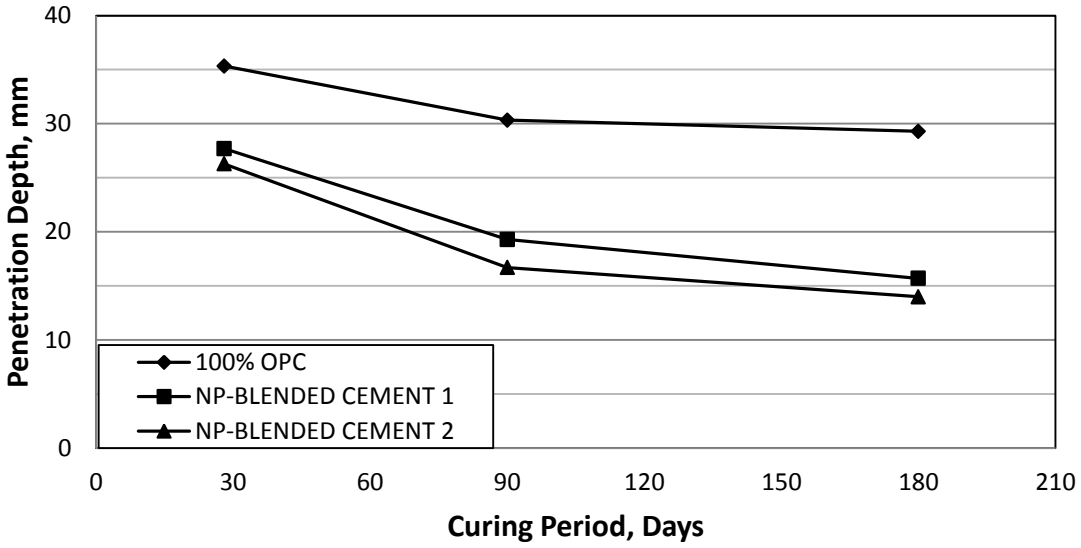

Figure 4-28: Depth of water penetration in specimens prepared with NP-blended Cements

4.3 Drying Shrinkage

The average drying shrinkage of specimens is summarized in Tables 4-4 through 4-7. Table 4-4 shows the drying shrinkage in OPC, all the three types of NP and the two NP-blended cements. After 210 days of observation, the drying shrinkage in specimens prepared with NPs and NP-blended cements showed less shrinkage than that of OPC specimens. The average drying shrinkage strain for OPC specimens, after 210 days of observation, was 448 microns and it was 382, 375, 368 microns for Type 1, 2 and 3 NPs, respectively. The average drying shrinkage strain for NP-blended cements was 418 and 415 microns.

Table 4-5 presents the drying shrinkage of the specimens associated with the physical activation of all three types of NPs (i.e. inclusion of SF in varying dosages). Addition of

SF into the mix increased the drying shrinkage of the specimens. For all the tree types of NPs, after 210 days of observation, the addition of 1% SF increased the drying shrinkage in comparison to specimens prepared with NP without the addition of SF. It was noted to be 391, 394 and 399 microns for all the three types of NPs. It was an increase of 2 to 8%, while this drying shrinkage strain was less than that of OPC. For the addition of 5% SF, an increase by 14 to 17% was noted in the drying shrinkage strain, in comparison to the specimens prepared with NP without SF. After 210 days of observation, the drying shrinkage strain of 5% SF specimens was 434, 437 and 430 microns, for all the three types of NPs. This drying shrinkage strain was slightly less than that of OPC, which was 448 microns.

Table 4-6 shows the drying shrinkage of the specimens incorporating HL along with NP as a chemical activator. The addition of 7% HL in the mix increased the drying shrinkage of the specimens. After 210 days of observation, the drying shrinkage of specimens with HL was 435 439 and 432 microns, for all the three types of NP, which was almost equal to that of OPC.

Table 4-7 shows the drying shrinkage of the specimens prepared with finer NPs. The use of finer NPs, also increased the drying shrinkage and after 210 days of observation whereby the drying shrinkage of finer NPs was 401, 403 and 398 microns which was about 5 to 8% higher than that of coarser NPs.

Table 4-4: Average drying shrinkage for OPC and three NP

Cementitious Materials	Average drying shrinkage strain, microns											
	Duration, Days											
	3	**7**	**14**	**21**	**28**	**45**	**60**	**90**	**120**	**150**	**180**	**210**
100% OPC	81	158	229	274	299	335	358	406	436	441	446	448
80% OPC + 20% Type 1 NP	89	152	214	256	299	325	342	365	374	381	382	382
80% OPC + 20% Type 2 NP	79	155	221	248	281	309	332	359	367	372	374	375
80% OPC + 20% Type 3 NP	72	140	206	237	271	293	326	354	363	370	370	368
NP-blended Cement 1	87	143	210	258	275	321	343	397	406	412	416	418
NP-blended Cement 2	91	145	219	263	282	328	358	389	401	411	417	415

Table 4-5: Average drying shrinkage of specimens of NP activated by SF

Cemetitious Materials	Average drying shrinkage strain, microns											
	Duration, Days											
	3	7	14	21	28	45	60	90	120	150	180	210
80% OPC + 20% Type 1 NP	89	152	214	256	299	325	342	365	374	381	382	382
20% Type 1 NP + 1% SF	71	133	201	221	271	289	326	347	388	393	391	391
20% Type 1 NP + 2% SF	78	138	209	228	283	297	331	355	397	401	403	403
20% Type 1 NP + 3% SF	71	132	218	243	291	306	348	363	403	417	421	419
20% Type 1 NP + 4% SF	80	139	217	248	294	312	351	368	401	422	424	424
20% Type 1 NP + 5% SF	79	149	223	266	297	321	355	381	413	428	432	434
80% OPC + 20% Type 2 NP	79	155	221	248	281	309	332	359	367	372	374	375
20% Type 2 NP + 1% SF	75	137	219	227	276	297	332	346	386	392	393	394
20% Type 2 NP + 2% SF	73	133	217	238	288	311	341	361	400	406	408	409
20% Type 2 NP + 3% SF	79	140	213	239	281	301	339	358	391	408	411	412
20% Type 2 NP + 4% SF	79	144	217	255	291	315	349	372	408	420	424	426
20% Type 2 NP + 5% SF	82	158	220	272	303	327	358	386	421	436	432	437
80% OPC + 20% Type 3 NP	72	140	206	237	271	293	326	354	363	370	370	368
20% Type 3 NP + 1% SF	78	142	212	229	281	305	337	349	393	397	399	399
20% Type 3 NP + 2% SF	81	141	213	234	279	304	338	359	401	404	402	405
20% Type 3 NP + 3% SF	76	136	220	249	285	308	344	366	398	413	417	417
20% Type 3 NP + 4% SF	74	140	215	251	289	310	347	364	402	417	421	421
20% Type 3 NP + 5% SF	76	152	213	259	293	322	348	376	404	422	428	430

Table 4-6: Average drying shrinkage of specimens of NP activated by HL

Cementitious Materials	Average drying shrinkage strain microns											
	Duration, Days											
	3	7	14	21	28	45	60	90	120	150	180	210
80% OPC + 20% Type 1 NP	89	152	214	256	299	325	342	365	374	381	382	382
73% OPC + 20% Type 1 NP + 7% HL	79	165	235	287	314	347	363	404	424	432	434	435
80% OPC + 20% Type 2 NP	79	155	221	248	281	309	332	359	367	372	374	375
73% OPC + 20% Type 2 NP + 7% HL	74	163	239	281	308	349	371	393	428	439	441	439
80% OPC + 20% Type 3 NP	72	140	206	237	271	293	326	354	363	370	370	368
73% OPC + 20% Type 3 NP + 7% HL	81	171	241	279	319	338	368	399	421	429	431	432

Table 4-7: Average drying shrinkage of specimens of Finer NP

Cementitious Materials	Average drying shrinkage strain, microns											
	Duration, Days											
	3	7	14	21	28	45	60	90	120	150	180	210
80% OPC + 20% Type 1 NP	89	152	214	256	299	325	342	365	374	381	382	382
80% OPC + 20% Type 1 NP (Fine)	87	164	219	268	310	329	364	385	394	399	397	401
80% OPC + 20% Type 2 NP	79	155	221	248	281	309	332	359	367	372	374	375
80% OPC + 20% Type 2 NP (Fine)	91	175	211	259	312	322	360	380	393	397	401	403
80% OPC + 20% Type 3 NP	72	140	206	237	271	293	326	354	363	370	370	368
80% OPC + 20% Type 3 NP (Fine)	83	159	207	273	317	328	357	374	389	393	396	398

4.3.1 Effect of Natural Pozzolan Addition as a Partial Replacement of OPC on Drying Shrinkage

Figure 4-29 shows the average drying shrinkage of OPC specimens and 20% replacement of OPC with all the three types of NP. All the specimens having 20% NP showed lower ultimate drying shrinkage than OPC. Up till 14 days, the shrinkage rate for all the specimens was same, thereafter, the rate of shrinkage for the specimens with NPs decreased. The ultimate average drying shrinkage strain for OPC specimens was 448 microns and it was 382, 375, 368 microns for Type 1, 2 and 3 NP, respectively. For specimens prepared with NPs the drying shrinkage was 15 to 18% less than that of OPC. Natural pozzolans tend to refine the pore structure and retain moisture for longer periods than OPC, which is why the drying shrinkage was observed to be lower in NP specimens than that of OPC. It is also reported by Sawan [62] that the specimens prepared with NP showed lower drying shrinkage than that of OPC when cured under water for 28 days. Further, concretes incorporating NP have less tendency to develop cracks due to drying shrinkage [63].

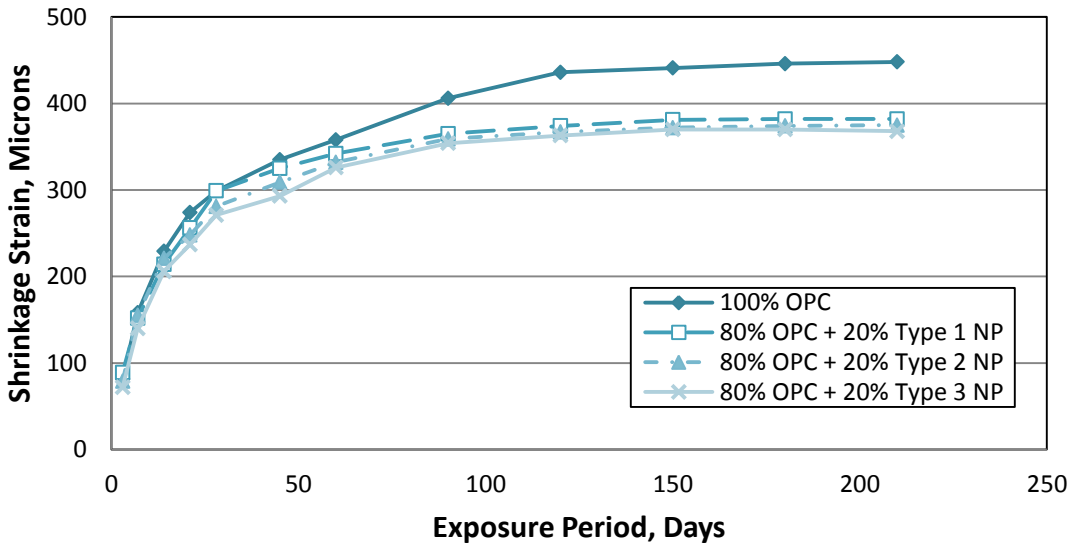

Figure 4-29: Drying shrinkage of OPC and three types of NP specimens

4.3.2 Drying Shrinkage of Physically-Activated Natural Pozzolan by Adding Silica Fume

Figures 4-30 through 4-32 show the drying shrinkage strain in the specimens with SF for activation of NP. For all the three types of NP used, by adding SF, the drying shrinkage increased with the increase in SF dosage from 1 to 5%. The highest shrinkage strain was observed in the specimen prepared with 20% Type 2 NP along with the addition of 5% SF. It was noted to be 437 microns. The lowest drying shrinkage strain of 391 microns was noted in the specimens prepared with 20% Type 1 NP and 1% SF. For all the three types of NPs the highest drying shrinkage strain was noted in specimens prepared with the addition of 5% SF, while the lowest drying shrinkage strain was noted in the specimens prepared with the addition of 1% SF. The drying shrinkage for all the other dosages lies in between 1% and 5% SF.

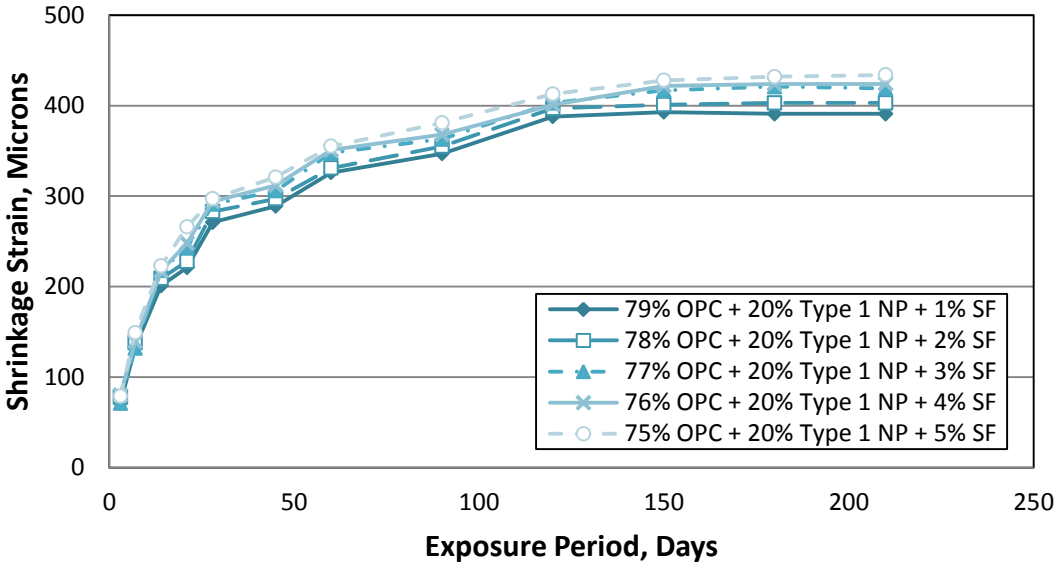

Figure 4-30: Drying shrinkage strain in specimens with SF and Type 1 NP

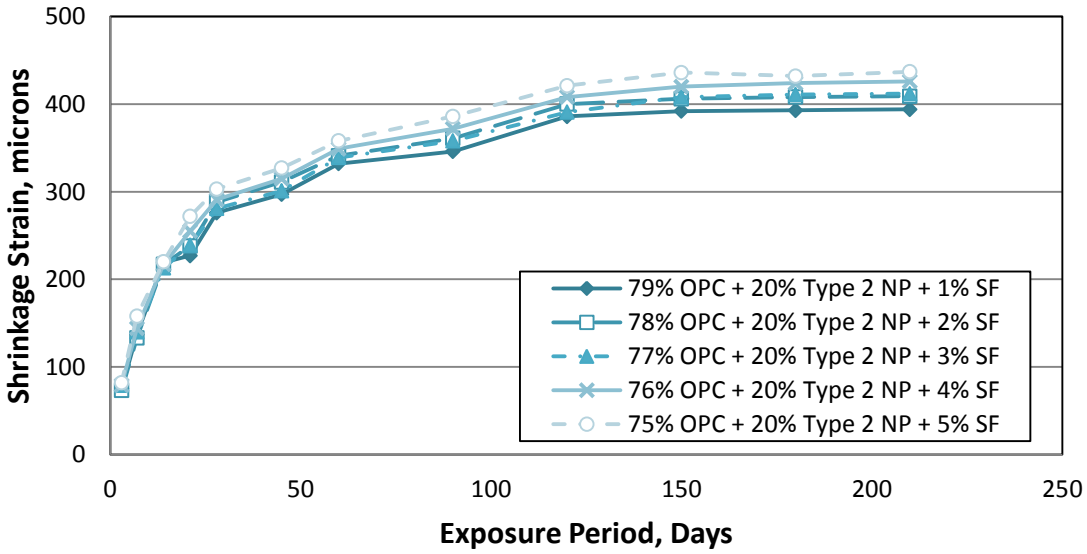

Figure 4-31: Drying shrinkage strain in specimens with SF and Type 2 NP

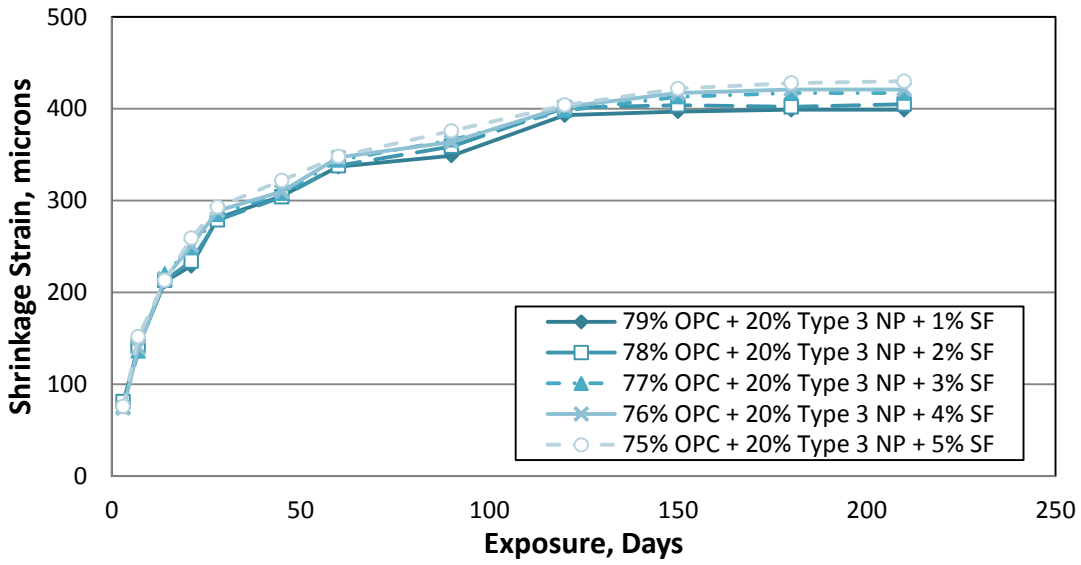

Figure 4-32: Drying shrinkage strain in specimens with SF and Type 3 NP

From the data in the above figures, it is established that for the three types of NP, the drying shrinkage strain increased with an increase in the SF dosage. Figures 4-33, 4-34 and 4-35 compare the drying shrinkage strain in the specimens in which SF was added to activate. In Figure 4-33, it is seen that the lowest drying shrinkage strain was in the specimens prepared 20% Type 1 NP, adding 1% SF increased the shrinkage strain by 2%. The Addition of 5% SF increased the drying shrinkage by 14% as compared to specimens of Type 1 NP without SF. However, the drying shrinkage strain of 5% SF was less than that of OPC. In fact, it was only 3% less than that of OPC. Figures 4-34 and 4-35 show the same trend for Type 2 and 3 NP, respectively. Addition of SF is known to increase the drying shrinkage strain of specimens. Whitting et al. [64] reported that the drying shrinkage strain of the specimens prepared with both SF and OPC was almost identical at later stages at early ages SF showed higher shrinkage strain than that of OPC. Al-Amoudi [65] evaluated the influence of specimens' dimensions and curing regime on shrinkage of

OPC and SF concretes and reported that the drying shrinkage strain in SF concrete specimens was always higher than that of OPC.

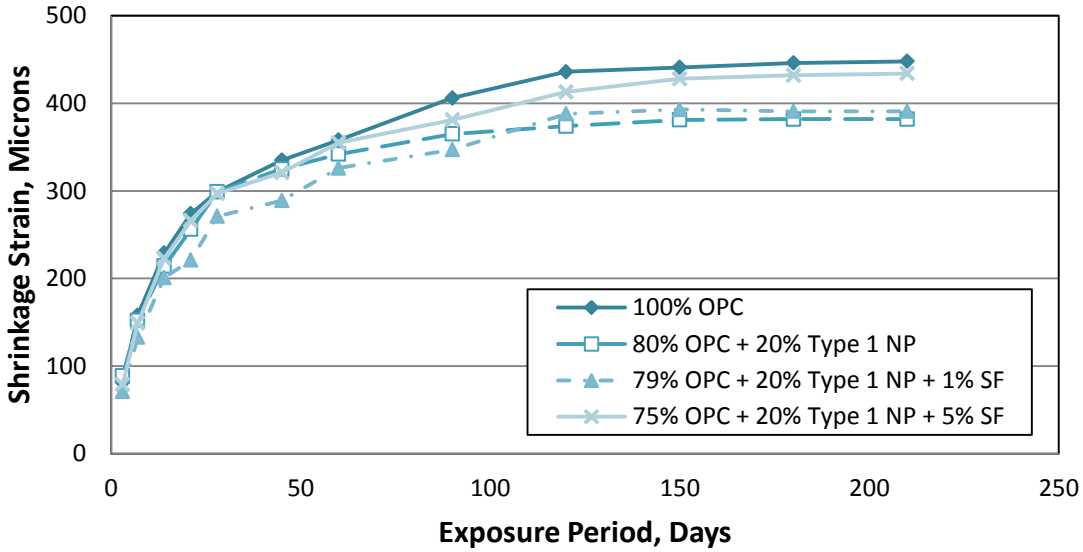

Figure 4-33: Comparison of drying shrinkage strain of OPC and SF with Type 1 NP

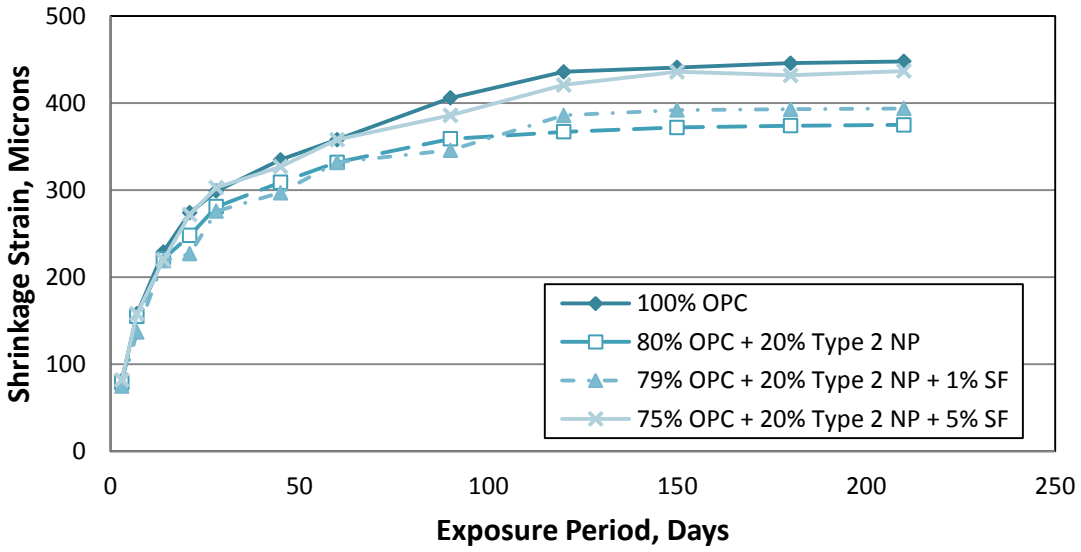

Figure 4-34: Comparison of drying shrinkage strain of OPC and SF with Type 2 NP

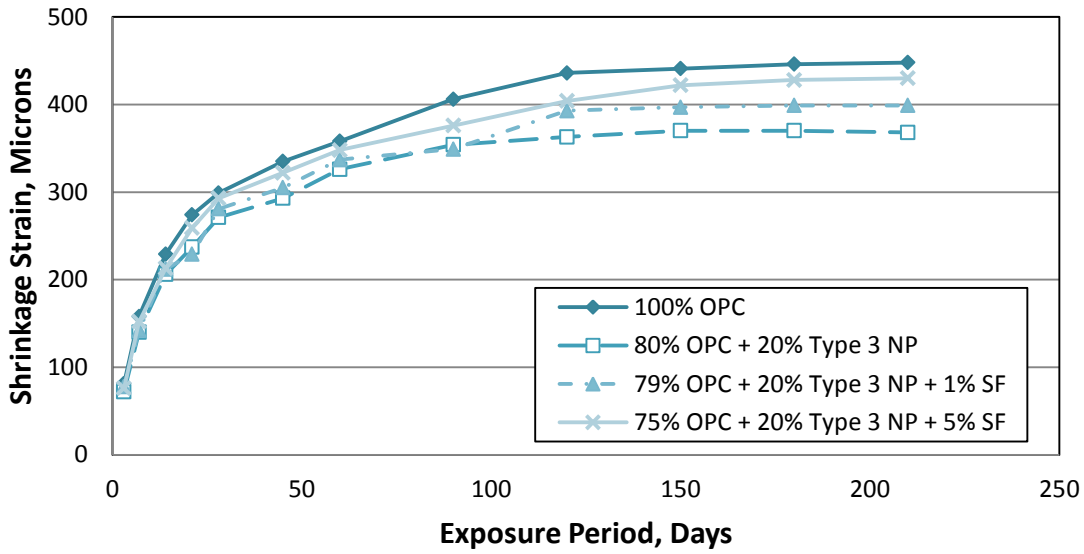

Figure 4-35: Comparison of drying shrinkage strain of OPC and SF with Type 3 NP

4.3.3 Drying Shrinkage of Chemically-Activated Natural Pozzolan by Adding Hydrated Lime

Figure 4-36 through 4-38 show the drying shrinkage of all the three types of NP activated by the addition of HL. The data there in indicate that the drying shrinkage increased with the period of exposure. At early ages, the drying shrinkage strain was similar to that of OPC specimens. At later stages, the drying shrinkage strain of the specimens prepared with Type 1 and 3 NPs are slightly less than that of OPC, as shown in Figures 4-36 and 4-38, while the drying shrinkage of the specimens prepared with Type 2 NP was almost equal to that of OPC, as shown in Figure 4-37. After 180 days of observation, the drying shrinkage strain in specimens of Type 1, 2 and 3 NPs prepared with the addition of HL was 434, 441 and 431 microns, respectively, compared to 446 microns in OPC

specimens. The high drying shrinkage strain of specimens with HL may be associated with the high rate of hydration which consumes most of the moisture within the mortar. It is reflected in the data presented in Table 4-1 where it is seen that at early periods of curing the compressive strengths of concretes with HL was just slightly less than that of OPC and at later periods of curing (i.e. after 90 days) the compressive strength of concretes with HL was higher than that of OPC.

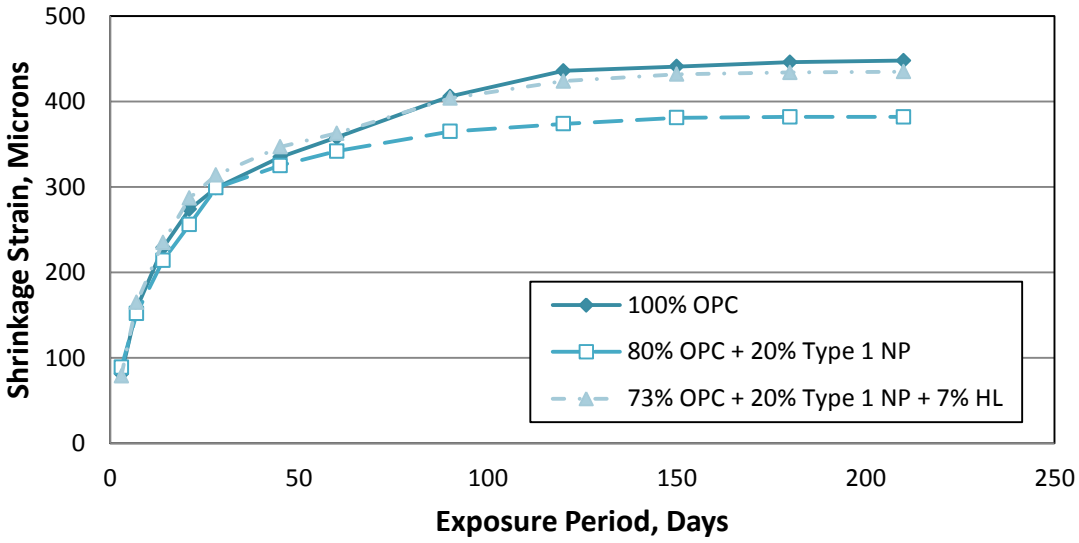

Figure 4-36: Drying shrinkage strain of specimens with HL and Type 1 NP

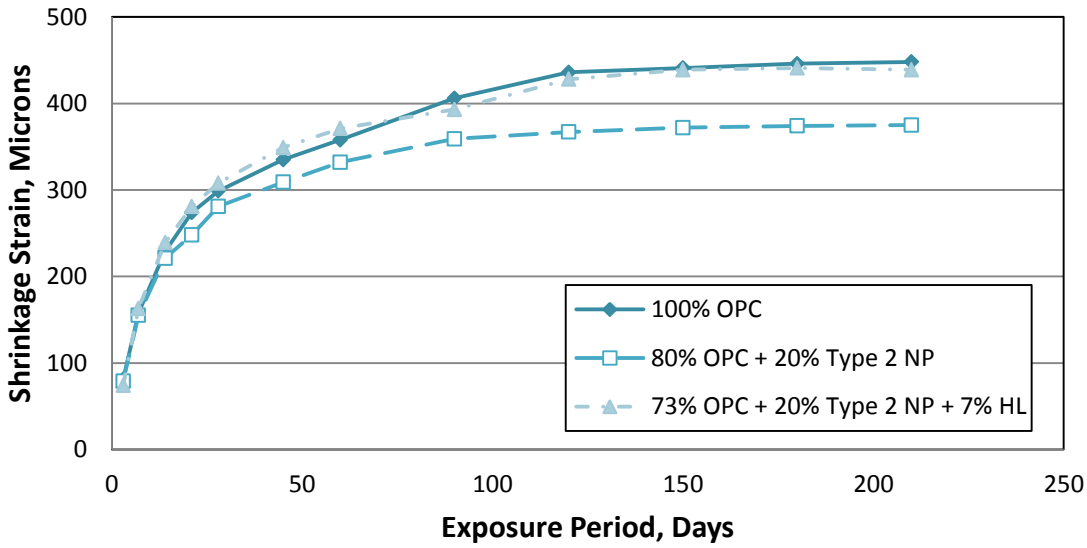

Figure 4-37: Drying shrinkage strain of specimens with HL and Type 2 NP

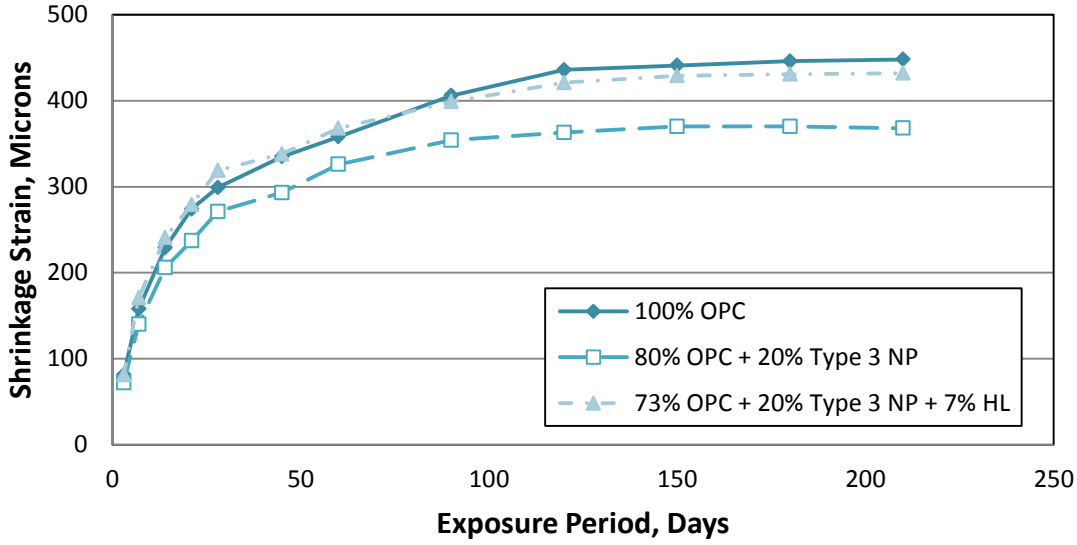

Figure 4-38: Drying shrinkage strain of specimens with HL and Type 3 NP

4.3.4 Drying Shrinkage of Mechanically-Activated Natural Pozzolan by Increasing the Fineness

Figures 4-39 through 4-41 show the drying shrinkage strain of all the three types of NPs with two finenesses. The drying shrinkage strain of all the three types of NP increased with the period of exposure. At later stages, the ultimate drying shrinkage strain for the specimens prepared with all three types of finer NP was less than that of OPC and slightly more than that of specimens of coarser NP.

After 210 days of observations, the drying shrinkage strain for all three types of finer NPs was in a range of 398 to 403 microns, compared to a range of 368 to 382 microns for coarser NPs and 448 microns of OPC. The drying shrinkage strain of finer NPs was 10 to 11% less than that of OPC and 5 to 7% higher than the strain of coarser NPs. This increase in the drying shrinkage is not significant, reflecting that increasing the fineness of these NPs had very little effect on the drying shrinkage of the mortar specimens.

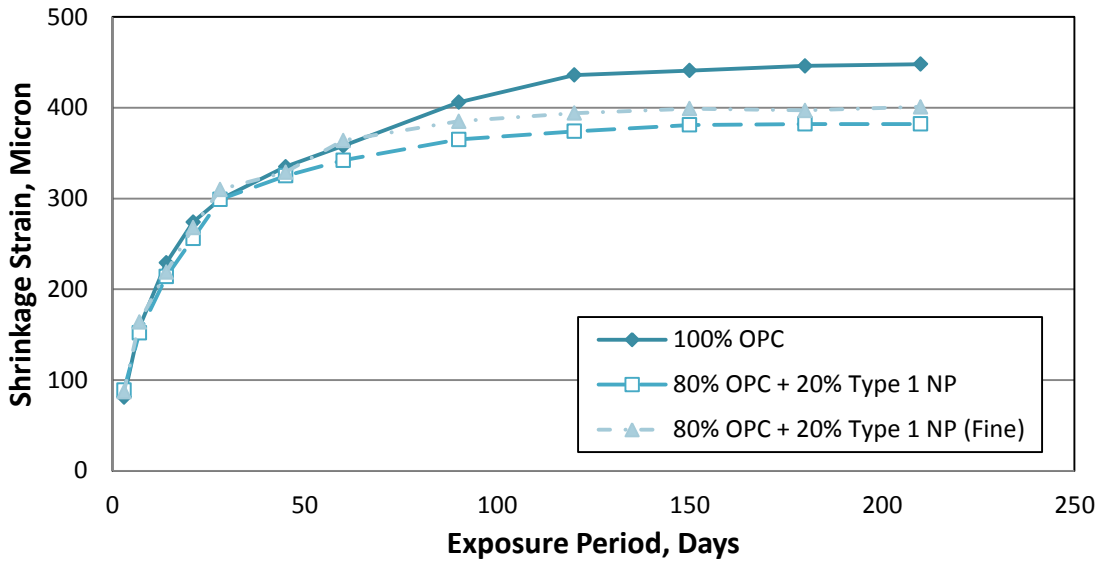

Figure 4-39: Drying shrinkage of specimens of finer Type 1 NP

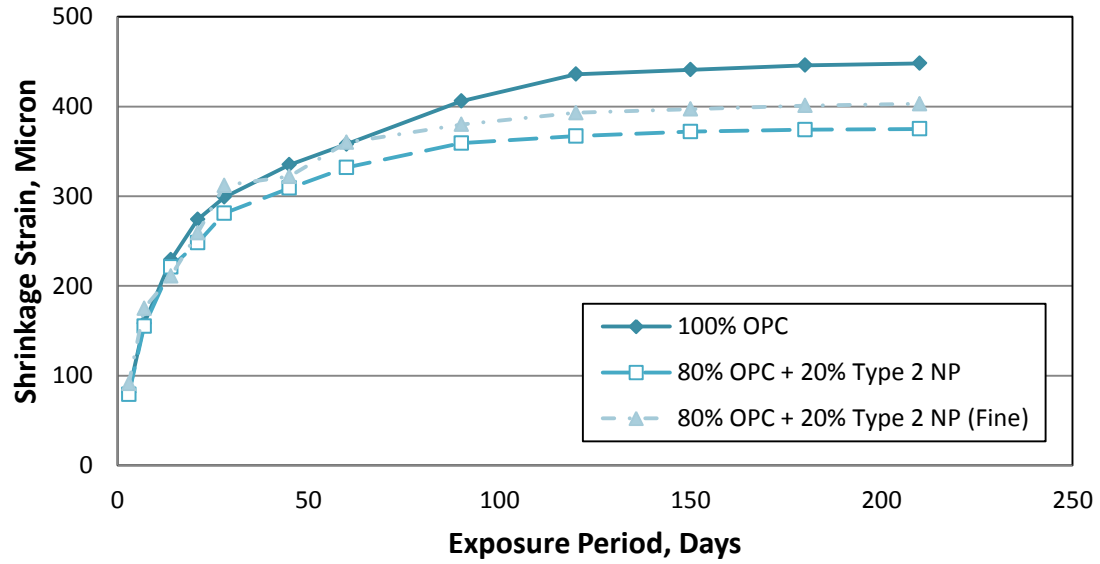

Figure 4-40: Drying shrinkage of specimens of finer Type 2 NP

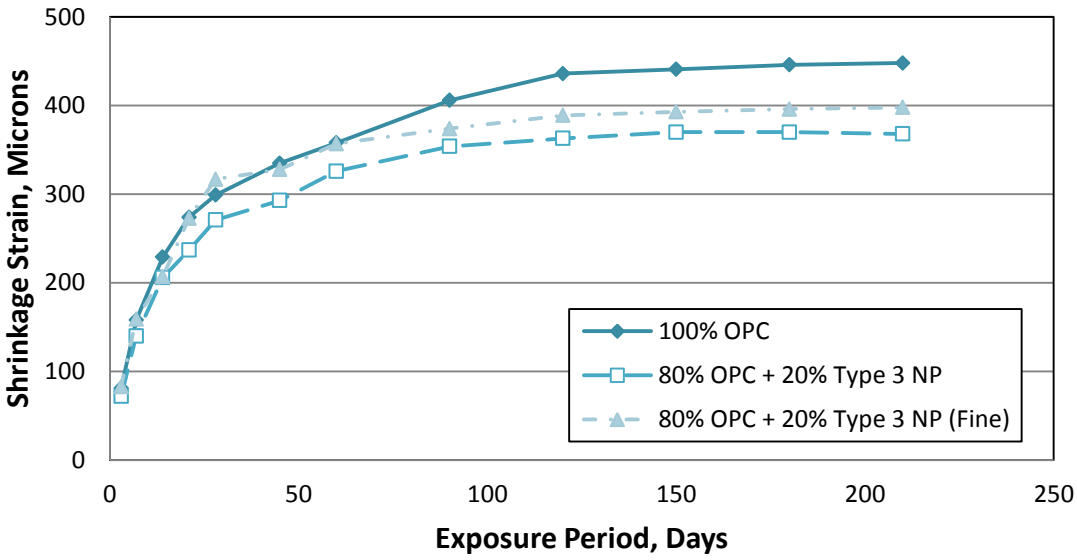

Figure 4-41: Drying shrinkage of specimens of finer Type 3 NP

4.3.5 Drying Shrinkage of NP-Blended Cements

Figure 4-42 shows the comparison of drying shrinkage of specimens prepared with two NP-blended cements with OPC. Both NP-blended cements behaved almost similarly and the ultimate drying shrinkage of NP-blended cements was less than that of OPC. After 210 days of observations, the drying shrinkage strain of two blended cements was 418 and 415 microns, compared to 448 microns of OPC, which is around 7% less than that of OPC. Also, the drying shrinkage strain of the specimens prepared with NP-blended cements was 8 to 11% higher than the strains in specimens prepared with three types of NPs. This may be because of different factors including the difference in fineness of NP-blended cements and three types of NPs and the amount of NP added in these blended

cements which may or may not be 20% (The amount of three types of NPs added in mixtures).

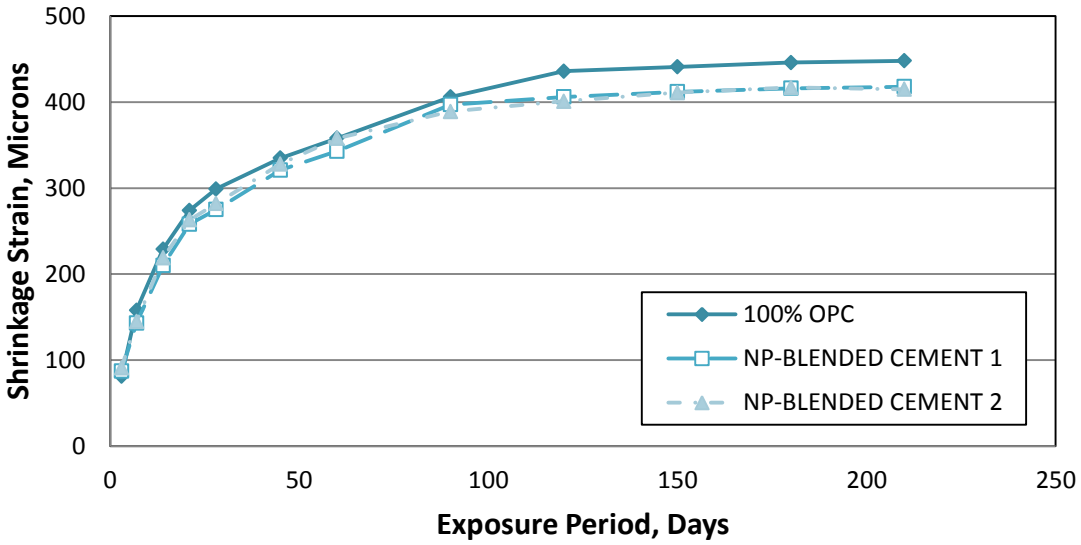

Figure 4-42: Drying shrinkage of specimens prepared with NP-blended cements

4.4 Chloride Diffusion

The chloride profiles for the different concrete types, including OPC, all three types of NP and their activation, are shown in Figures 4-43 through 4-56. The chloride concentrations were determined after exposing the concrete specimens to 5% NaCl solution for six months. The chloride profiles were utilized to determine the chloride diffusion coefficients according to Fick's second law of diffusion as explained in Section 3.5.4 in the chapter on the Experimental Program (Chapter 3).

4.4.1 Chloride Diffusion of Natural Pozzolan Concrete

Figure 4-43 shows the chloride profile for OPC and three types of NP as a partial replacement of OPC. The chloride concentration in NP specimens was less than that in OPC at all depths. Further, the concentration of chloride decreased with the depth of the specimen from the diffusing surface. At 10 mm depth, the chloride concentration for OPC was 0.13% by weight of concrete while the concentration in Type 1, 2 and 3 NP were 0.082, 0.08 and 0.071, respectively, at the same depth. Addition of supplementary cementing material such as natural pozzolan helps reduce the permeability of concrete to chloride ions [66]. Kaid et al. [67] reported that addition of Algerian natural pozzolan helped reduce the chloride diffusion in concrete.

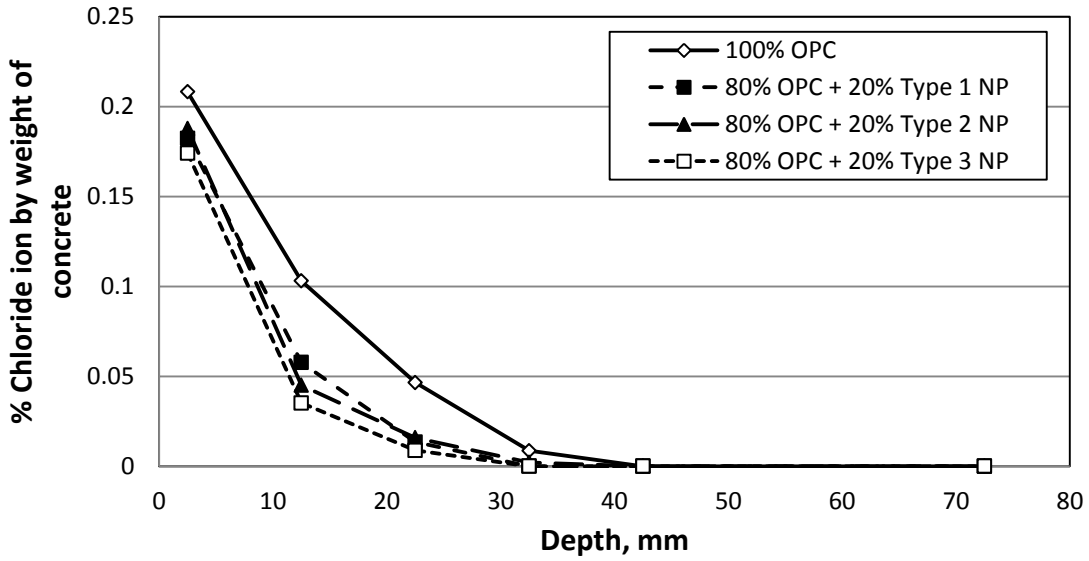

Figure 4-43: Chloride profile in OPC and NP specimens

4.4.2 Chloride Diffusion of Physically-Activated Natural Pozzolan

Figures 4-44 through 4-46 illustrate the chloride profiles in Types 1, 2 and 3 NP concretes, respectively. The data in Figure 4-44 shows that the chloride concentration decreased with an increase in the SF content. The data for Type 2 and 3 NPs follow a similar trend as seen in Figures 4-45 and 4-46. The highest chloride concentration at 10 mm depth was observed in the specimens prepared with 20% Type 2 NP and 1% SF which was 0.0575% by weight of concrete, while the lowest chloride concentration was noted in the specimens prepared with 20% Type 3 NP and 5% SF which was 0.0075% by weight of concrete. Addition of any pozzolan, especially silica fume, which is a super-pozzolanic material into the mix, significantly decreases the permeability of concrete [62, 66]. In this study it is reflected by low depths of water penetration and less chloride ingress in the specimens prepared with SF in comparison to OPC.

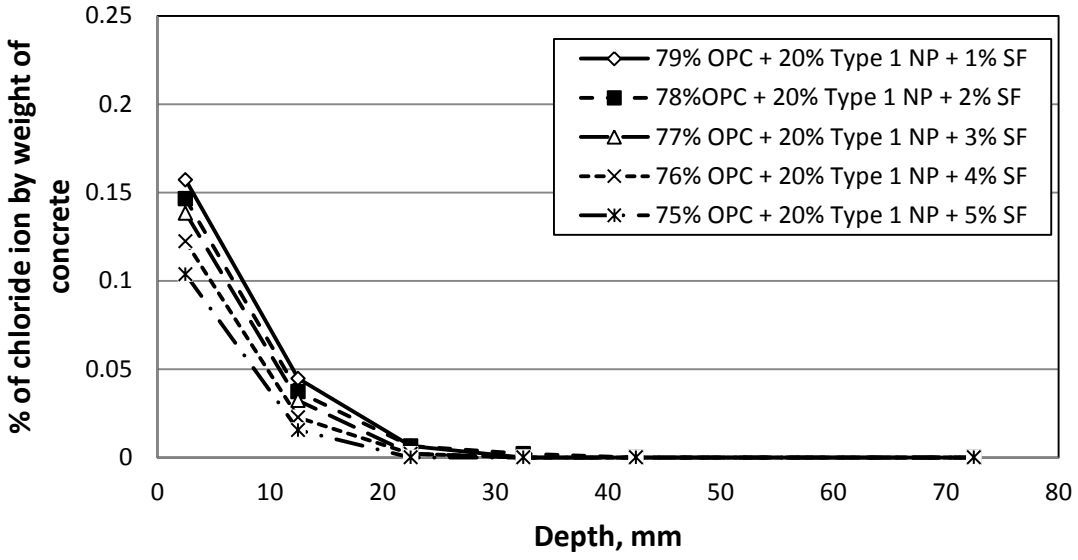

Figure 4-44: Chloride profile of Type 1 NP plus SF

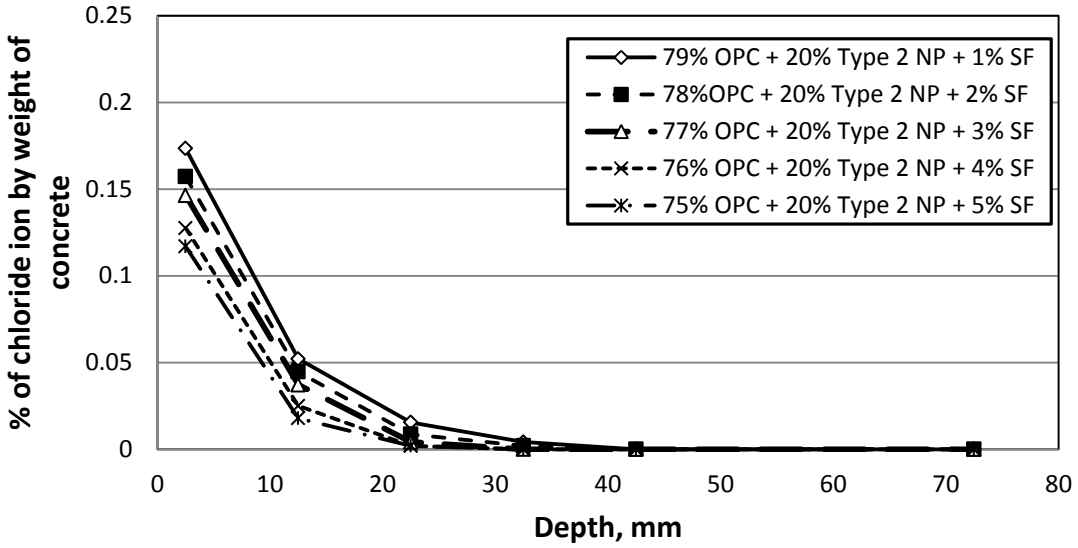

Figure 4-45: Chloride profile of Type 2 NP plus SF

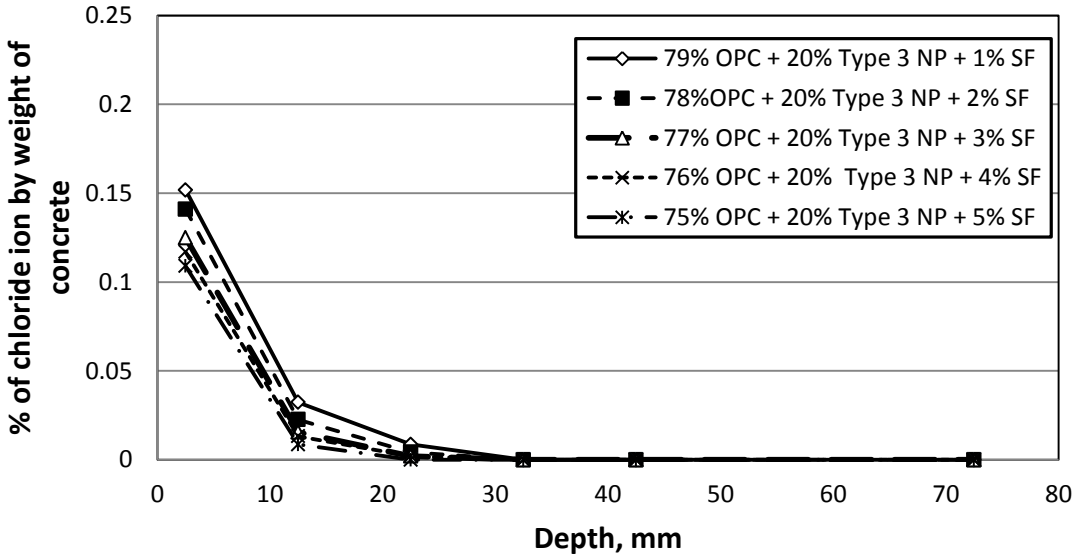

Figure 4-46: Chloride profile of Type 3 NP specimens plus SF

From the figures above, it was clear that the chloride concentration decreases by increasing the SF content in all the three types of NP. Figure 4-47 shows the comparison between the chloride concentration of specimens prepared with SF and Type 1 NP

specimens without SF and OPC. It is seen that the chloride concentration of the specimens prepared with 20% Type 1 NP and 1% SF is lower than that of Type 1 NP specimens. Also, it is lower than that in OPC. Specimens prepared with 5% SF and 20% Type 1 NP exhibited that lowest chloride concentrations. The chloride concentration in Type 2 and 3 NPs specimens with 1% SF and 20% NP was almost similar to that of specimens with 20% NP without SF. However, the chloride concentration in specimens with 5% SF with 20% NP was the lowest, as shown in Figures 4-48 and 4-49. Pargar et al. [68] reported that the depth of chloride diffusion decreased as the replacement of SF increased. Shekarchi [69] reported that the maximum reduction in the chloride diffusion co-efficient was observed with the SF replacement of 7.5%. The reduction in chloride diffusion increased with the increase of SF content up till 7.5%.

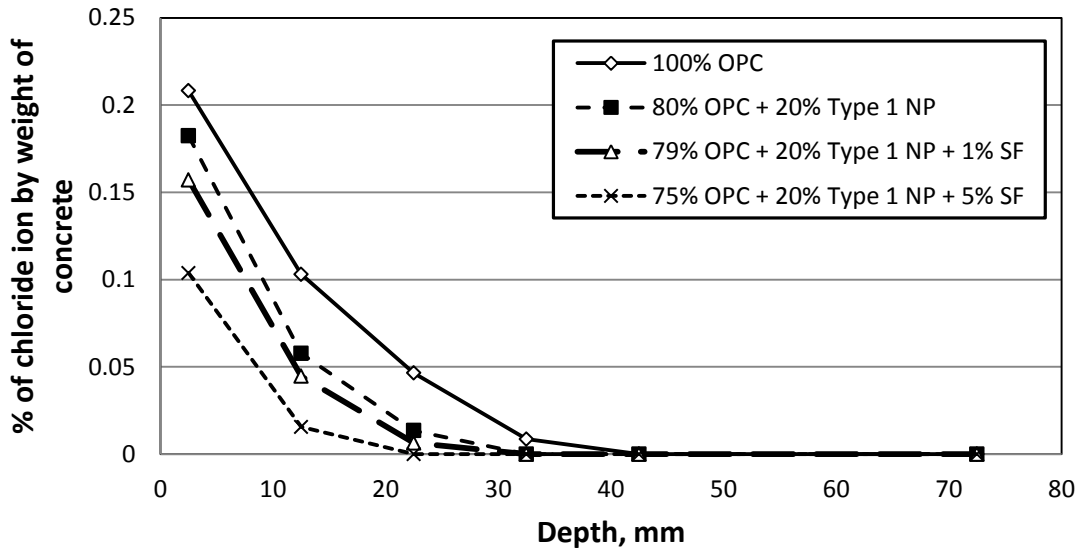

Figure 4-47: Comparison of chloride profile of OPC with Type 1 NP plus SF

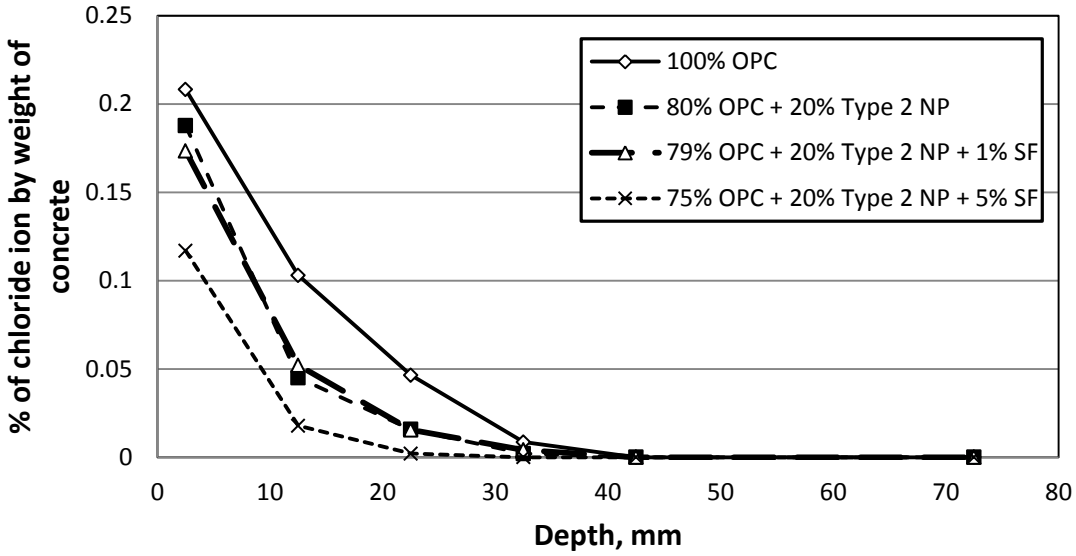

Figure 4-48: Comparison of chloride profile of OPC with Type 2 NP plus SF

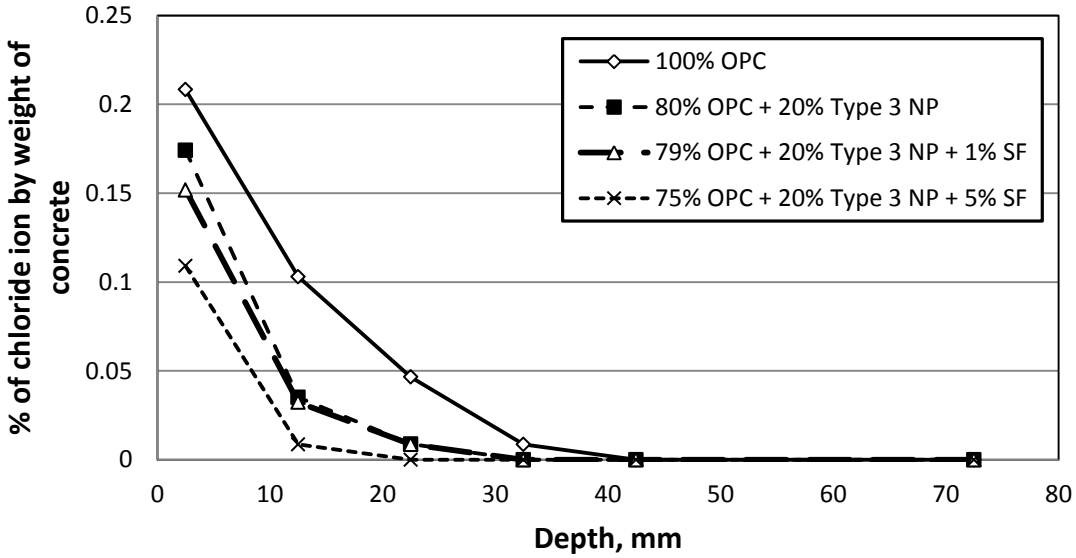

Figure 4-49: Comparison of chloride profile of OPC with Type 3 NP plus SF

4.4.3 Chloride Diffusion of Chemically-Activated Natural Pozzolan

Figures 4-50 through 4-52 show the chloride profile for the specimens prepared with 20% Types 1, 2 and 3 NP, respectively. In addition to the 20% NP, the 7% HL was also used as a chemical activator for NP. These specimens are also compared with OPC and NP specimens. The addition of HL to 20% Type 1 NP decreased the chloride concentrations at all levels, as seen in Figure 4-50. This is also true for Type 3 NP as shown in Figure 4-52. For Type 2 NP, the addition of HL helped to decrease chloride concentration at surface but at depths of more than 10 mm, the addition of HL did not show improvement and it is comparable to that for the specimens with 20% Type 2 NP without HL, as may be seen in Figure 4-51. Ghrici [16] studied ternary mix incorporating natural pozzolan and limestone powder. He reported that with the inclusion of natural pozzolan and limestone powder, the resistance to chloride ion penetration increased, compared to that of OPC control mix.

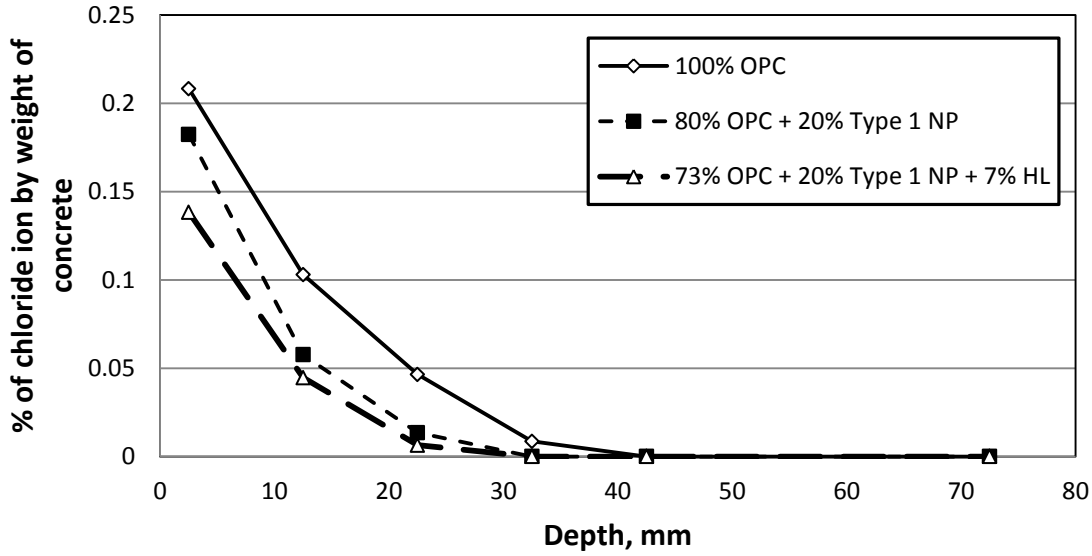

Figure 4-50: Chloride profile of specimens with Type 1 NP plus HL

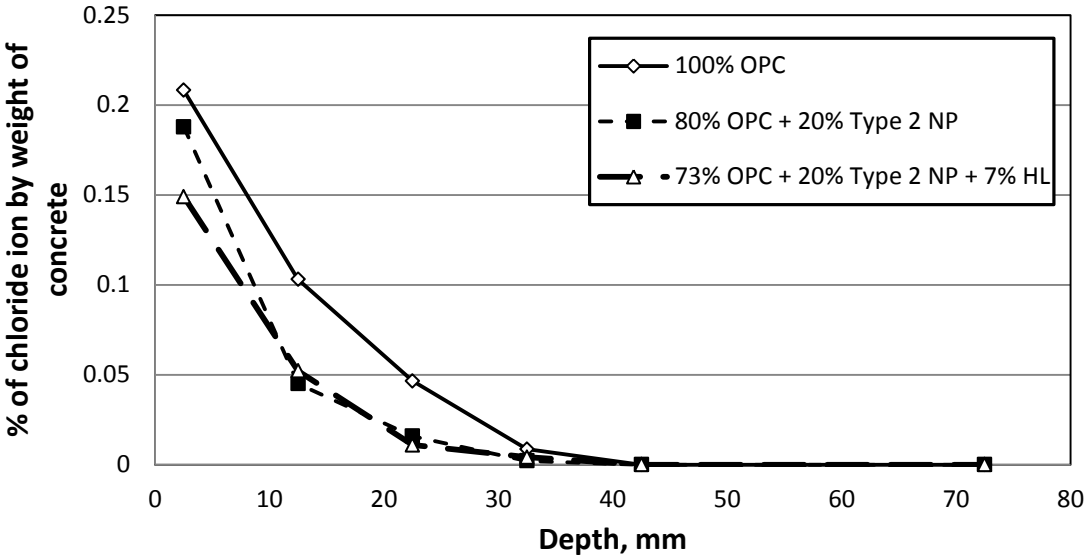

Figure 4-51: Chloride profile of specimens with Type 2 NP plus HL

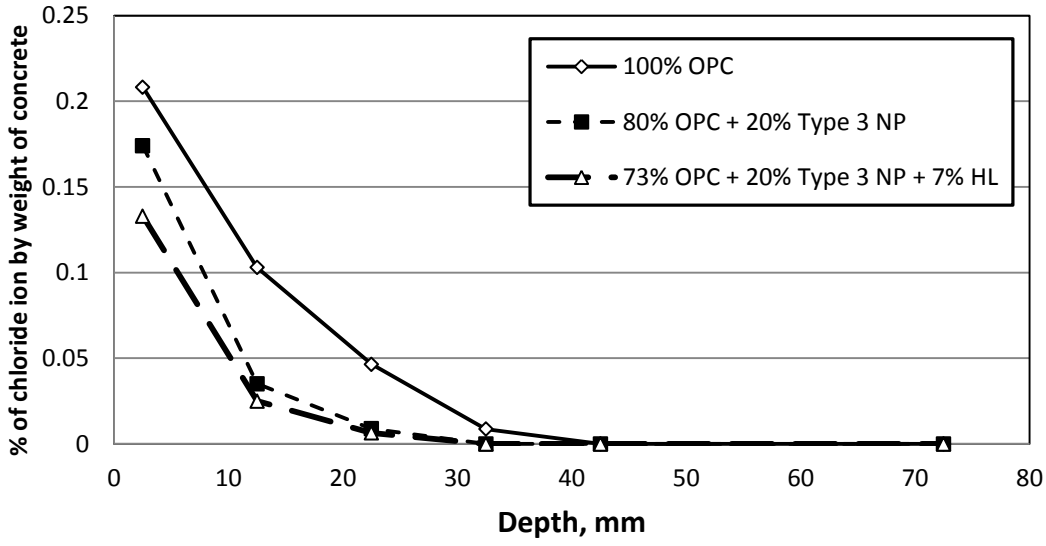

Figure 4-52: Chloride profile of specimens with Type 3 NP plus HL

4.4.4 Chloride Diffusion of Mechanically-Activated Natural Pozzolan

Figures 4-53, 4-54 and 4-55 show the chloride profile for the specimens prepared with finer Type 1, 2 and 3 NPs, respectively. These profiles are compared with those for the specimens prepared with coarser NP and OPC. These figure show that there was a slight improvement in all the types of NP as the fineness of NP was increased. The chloride concentration in finer Type 1, 2 and 3 NPs specimens at 10 mm depth was 0.065%, 0.072% and 0.052%, respectively, compared to 0.082%, 0.08% and 0.071% in coarse NPs and 0.13% in OPC specimens. Fine NP, compared to coarse NP, has larger surface area and it is slightly more reactive and has more packing ability making concrete denser, which is why the chloride diffusion decreased for all the three types of NP.

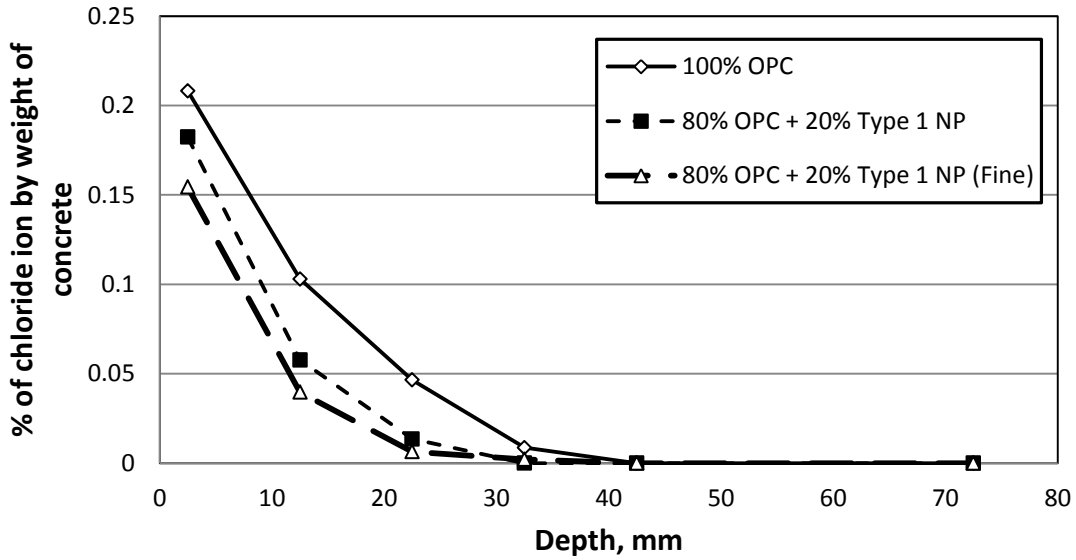

Figure 4-53: Chloride profile of finer Type 1 NP

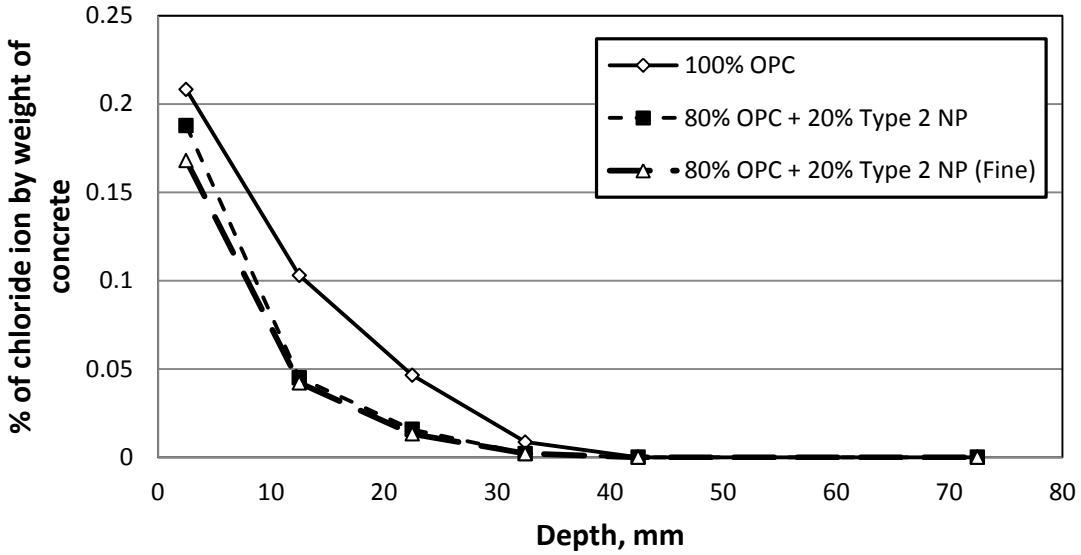

Figure 4-54: Chloride profile of finer Type 2 NP

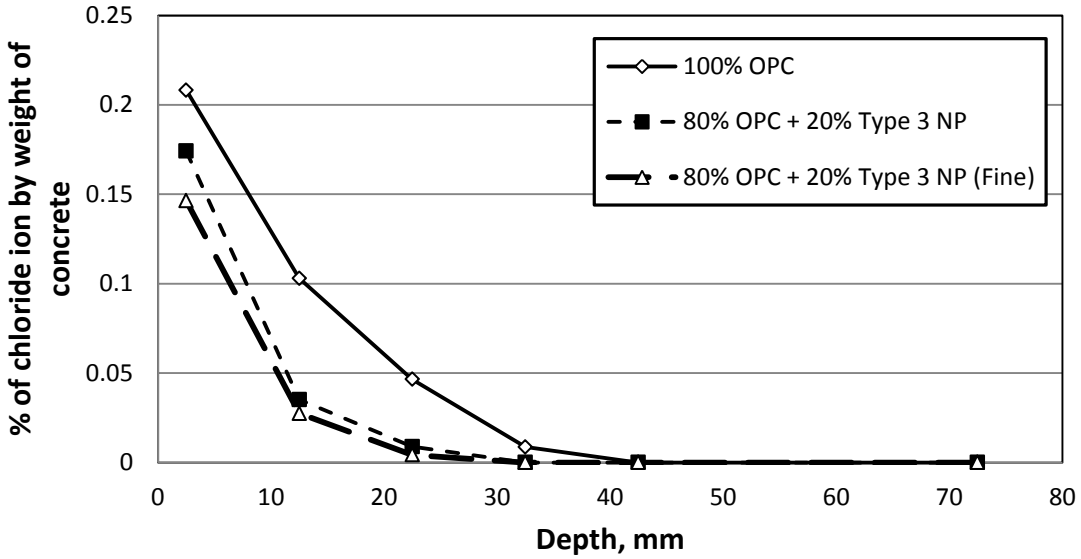

Figure 4-55: Chloride profile of finer Type 3 NP

4.4.5 Chloride Diffusion of NP-Blended Cements

The chloride concentration in the blended cements was less than that in OPC, as shown in Figure 4-56. For both the blended cements the chloride concentration at 10 mm depth was almost equal to 0.05% compared to 0.13% in OPC specimens. As discussed in Section 4.4.1 the addition of natural pozzolan decreases the chloride diffusion in concrete specimens. Similarly, less chloride diffusion was observed in NP-blended cement concrete specimens. Mohammad et al. [70] reported that chloride ingress in blended cement concrete specimens was less than that of OPC specimens.

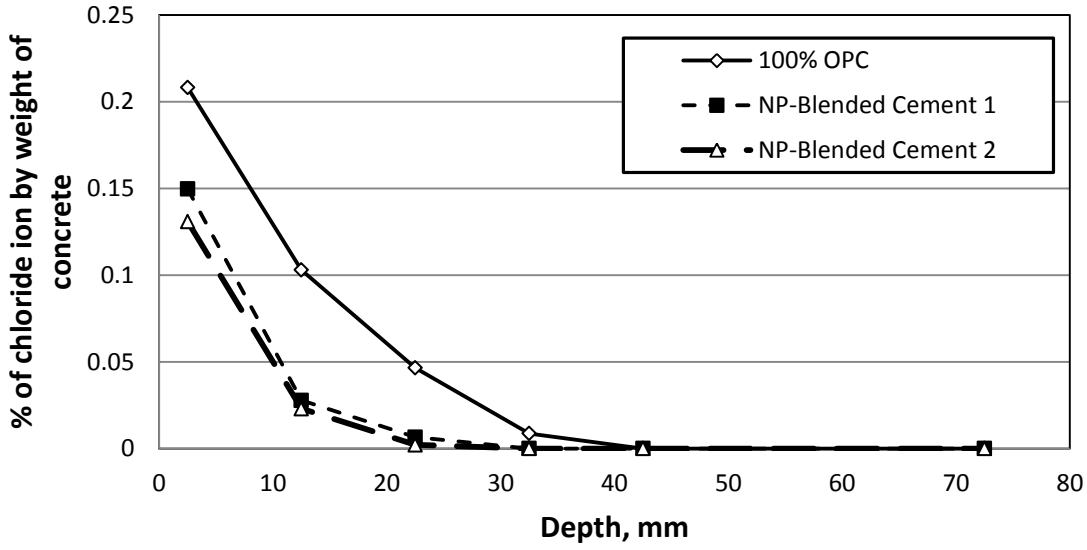

Figure 4-56: Chloride profile of specimens prepared with NP-Blended cements

4.4.6 Chloride Diffusion Coefficients

Tables 4-8 through 4-11 summarize the chloride diffusion coefficients for all the specimens which were exposed to 5% NaCl solution for six months. The chloride diffusion coefficients were calculated using Fick's second law of diffusion, which was applied to chloride profiles shown in Figures 4-43 trough 4-56.

Table 4-8 shows the diffusion coefficients of OPC, all three types of NP and both NP-blended cements. OPC has the highest coefficient of diffusion while the addition of NP (All types) caused a reduction in chloride diffusion coefficient. However, the reduction in the diffusion coefficient was the highest in the specimens prepared with NP-blended cement. Tables 4-9 through 4-11 show the chloride diffusion coefficients of all three types of NPs, along with the activation methods. In all three types of NP, addition of SF has clearly decreased the diffusion coefficient. The addition of HL or increasing the fineness of NP also helped in decreasing the diffusion coefficient.

Table 4-9 shows the chloride diffusion coefficients of specimens prepared with Type 1 NP. Addition of NP resulted in 48.1% reduction in chloride diffusion coefficients as compared to OPC. For this group the maximum reduction in the diffusion coefficient was noted when 5% SF was also added into the mix along with 20% Type 1 NP. It was noted to be 75.8%. Addition of HL and increasing the fineness of Type 1 NP resulted in the reduction of chloride diffusion coefficient by 54.7 and 60.2%, respectively.

Table 4-10 shows the chloride diffusion coefficients of specimens prepared with Type 2 NP. Addition of NP resulted in 57.7% reduction in chloride diffusion coefficients as

compared to OPC. As in the case of Type 1 NP, for this group as well, the maximum reduction in the diffusion coefficient was noted when 5% SF was also added into the mix along with 20% Type 2 NP. It was noted to be 75.5%. Addition of HL and increasing the fineness of Type 1 NP resulted in the reduction of chloride diffusion coefficient by 66.8 and 52.9%, respectively.

Table 4-11 shows the chloride diffusion coefficients of specimens prepared with Type 3 NP. Addition of NP resulted in 62.7% reduction in chloride diffusion coefficients as compared to OPC. As discussed above, in the case of other two Types of NP, for this group as well, the maximum reduction in the diffusion coefficient was noted when 5% SF was also added into the mix along with 20% Type 3 NP. It was noted to be 85.6%. Addition of HL and increasing the fineness of Type 1 NP resulted in the reduction of chloride diffusion coefficient by 67.9 and 66.3%, respectively.

Chloride diffusion coefficient highly depends on the difference of the concentration of chloride at the surface of the specimens and at a certain specified depth, in this study 10 mm. Greater the difference, lower would be the chloride diffusion coefficient. Concretes with low permeability decrease the chloride ion ingress resulting in low chloride concentrations inside the specimens compared to the chloride concentrations at the surface. It is discussed in Sections 4.4.1 through 4.4.5 that the addition of pozzolanic material and use of blended cements reduce the permeability of concrete, resulting in low chloride concentrations at the depth 10 mm. These values of chloride diffusion coefficients reflect the chloride concentration profiles shown in Figures 4-43 through 4-56.

Table 4-8: Chloride diffusion coefficient for OPC, NP and NP-blended cements

Cementitious Materials	Chloride Diffusion Coefficient x 10^{-8} cm^2/s	Reduction in Diffusion Coefficient, %
100% OPC	6.11	-
NP-BLENDED CEMENT 1	2.19	64.2
NP-BLENDED CEMENT 2	1.85	69.7
80% OPC + 20% Type 1 NP	3.17	48.1
80% OPC + 20% Type 2 NP	2.55	57.7
80% OPC + 20% Type 3 NP	2.28	62.7

Table 4-9: Chloride diffusion coefficient for OPC, Type 1 NP and its activators

Cementitious Materials	Chloride Diffusion Coefficient x 10^{-8} cm^2/s	Reduction in Diffusion Coefficient, %
100% OPC	6.11	-
80% OPC + 20% Type 1 NP	3.17	48.1
79% OPC + 20% Type 1 NP + 1% SF	2.80	54.2
78% OPC + 20% Type 1 NP + 2% SF	2.43	60.3
77% OPC + 20% Type 1 NP + 3% SF	2.09	65.8
76% OPC + 20% Type 1 NP + 4% SF	1.59	74.0
75% OPC + 20% Type 1 NP + 5% SF	1.48	75.8
73% OPC + 20% Type 1 NP + 7% HL	2.77	54.7
80% OPC + 20% Type 1 NP (FINE)	2.43	60.2

Table 4-10: Chloride diffusion coefficient for OPC, Type 2 NP and its activators

Cementitious Materials	Chloride Diffusion Coefficient x 10^{-8} cm^2/s	Reduction in Diffusion Coefficient, %
100% OPC	6.11	-
80% OPC + 20% Type 2 NP	2.55	57.7
79% OPC + 20% Type 2 NP + 1% SF	2.88	52.9
78% OPC + 20% Type 2 NP + 2% SF	2.84	53.5
77% OPC + 20% Type 2 NP + 3% SF	2.25	63.2
76% OPC + 20% Type 2 NP + 4% SF	1.96	67.9
75% OPC + 20% Type 2 NP + 5% SF	1.50	75.5
73% OPC + 20% Type 2 NP + 7% HL	2.03	66.8
80% OPC + 20% Type 2 NP (FINE)	2.84	52.9

Table 4-11: Chloride diffusion coefficient for OPC, Type 3 NP and its activators

Cementitious Materials	Chloride Diffusion Coefficient x 10^{-8} cm^2/s	Reduction in Diffusion Coefficient, %
100% OPC	6.11	-
80% OPC + 20% Type 3 NP	2.28	62.7
79% OPC + 20% Type 3 NP + 1% SF	2.03	66.8
78% OPC + 20% Type 3 NP + 2% SF	1.78	70.9
77% OPC + 20% Type 3 NP + 3% SF	1.68	72.5
76% OPC + 20% Type 3 NP + 4% SF	1.37	77.6
75% OPC + 20% Type 3 NP + 5% SF	0.88	85.6
73% OPC + 20% Type 3 NP + 7% HL	1.96	67.9
80% OPC + 20% Type 3 NP (FINE)	2.06	66.3

4.5 Reinforcement Corrosion

Reinforced concrete specimens prepared with OPC, all the three Types of NP with two finenesses, all the three types of NP with addition of SF and HL and NP-blended cements were partially immersed in 5% sodium chloride solution and the corrosion potentials

were measured periodically up to 300 days. The test results for each type of concrete are plotted as a typical exposure time versus corrosion potential curves, as shown in Figures 4-57 through 4-70. The corrosion potential curves were utilized to assess the time to initiation of reinforcement corrosion using the ASTM C 876 criterion. As per this standard, if the measured corrosion potentials are less than –270 mV with reference to saturated calomel electrode (SCE), then there is 90% probability of initiation of reinforcement corrosion. The time to initiation of reinforcement corrosion is summarized in Tables 4-12 through 4-18.

4.5.1 Effect of Natural Pozzolan Addition as a Partial replacement of OPC on Time to Initiation of Corrosion

The data in Table 4-12 show the time to initiation of corrosion in OPC with 20% NP. This time for initiation of corrosion is calculated using the data in Figure 4-57. The time to corrosion in NP concrete was more than that in OPC. The time to corrosion in OPC was 177 days while it was 234 to 238 days in NP concretes. Moreover, the time to initiation of corrosion was almost the same in all the three types of pozzolanic concretes. Najimi [19] and Fajardo [40] reported that the addition of natural pozzolan had a significant improvement in the corrosion-resistance of concrete.

Table 4-12: Time to initiation of reinforcement corrosion in OPC and NP concrete

Cementitious Materials	Time to Initiation of Corrosion, Days
100% OPC	177
80% OPC+ 20% Type 1 NP	237
80% OPC+ 20% Type 2 NP	238
80% OPC+ 20% Type 3 NP	234

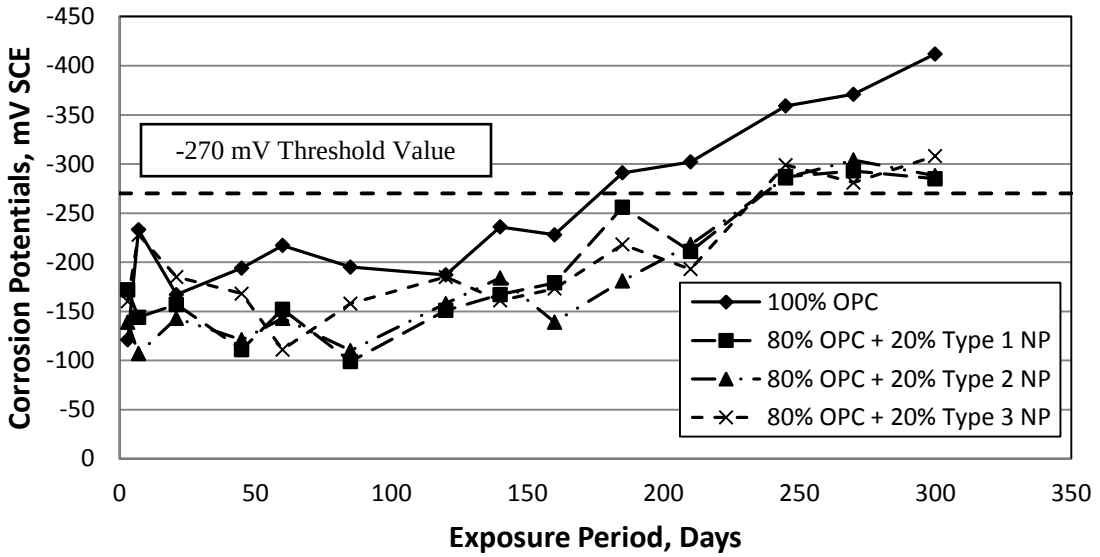

Figure 4-57: Corrosion potentials on steel in OPC and NP concrete

4.5.2 Effect of Physical Activation of Natural Pozzolan Time to Initiation of Corrosion

The data in Tables 4-13, 4-14 and 4-15 show the time to initiation of corrosion in the specimens prepared with Type 1, 2 and 3 NPs, respectively, with the addition of varying quantity of SF (1-5%). The corrosion potentials for these specimens are shown in Figures 4-58 through 4-63. Figures 4-58 through 4-60 show the variation in potentials with the

change in SF content for Type 1, 2 and 3 NPs, while Figures 4-61 through 4-63 show the comparison of the various types of pozzolan with OPC.

The data in Table 4-13 show that there was a slight improvement in the corrosion resistance when 1% and 2% SF is added with 20% Type 1 NP. The time to initiation of corrosion in steel within the Type 1 NP specimens prepared with 1 and 2% SF was 254 and 265 days, respectively, compared to 237 days in Type 1 NP concrete without SF and 177 days in OPC specimens. With the increase in SF content beyond 2%, no corrosion initiation was detected. Type 2 and 3 NPs, as shown in Tables 4-14 and 4-15, exhibited higher improvement in time to initiation of corrosion when SF was added, compared to Type 1 NP.

For Type 2 NP addition of 1% SF increased the time to initiation of corrosion to 303 days compared to 177 days for OPC. With the addition of 2% and more SF, no initiation of corrosion was observed in specimens of Type 2 NP up till 300 days of observation.

For Type 3 NP addition of 1% SF increased the time to initiation of corrosion to 310 days compared to 177 days for OPC. Similar to the behavior of Type 2 NP, with the addition of 2% and more SF, no initiation of corrosion was observed in specimens of Type 3 NP up till 300 days of observation.

From Figures 4-58 through 4-60 show that with the increase in the SF content the corrosion potentials decreased with the highest potentials noted when 1% SF is added to all three types of NP, while lowest potentials were noted when 5% SF was added to all three types of NP. Figure 4-58 shows that only the graphs of specimens prepared with 1%

and 2% SF crossed the threshold value of -270 mV up till 300 days of observation. While for Type 2 and 3 NP, only the specimens prepared with 1% SF crossed the threshold, as shown in Figures 4-59 and 4-60. Most of the problems associated to the corrosion of steel reinforcement in concrete in Arabian Gulf are chloride-induced [71]. As discussed in Section 4.4, research show that with the increase of SF content in concrete, the permeability of chloride ion in concrete decreased [63, 66, 68, 69]. This reflects in less corrosion in steel embedded in concrete prepared with SF than OPC.

Figures 4-61 through 4-63 show the comparison of corrosion potentials of specimens prepared with 1 and 5% SF with OPC. It is seen in these Figures that for all three Types of NPs, the corrosion potentials of specimens prepared with SF were less than that of OPC.

Table 4-13: Time to initiation of reinforcement corrosion in Type 1 NP plus SF

Cementitious Materials	Time to Initiation of Corrosion, Days
100% OPC	177
80% OPC + 20% Type 1 NP	237
79% OPC + 20% Type 1 NP + 1% SF	254
78% OPC + 20% Type 1 NP + 2% SF	265
77% OPC + 20% Type 1 NP + 3% SF	No initiation
76% OPC + 20% Type 1 NP + 4% SF	No initiation
75% OPC + 20% Type 1 NP + 5% SF	No initiation

Table 4-14: Time to initiation of reinforcement corrosion in Type 2 NP plus SF

Cementitious Materials	Time to Initiation of Corrosion, Days
100% OPC	177
80% OPC + 20% Type 2 NP	238
79% OPC + 20% Type 2 NP + 1% SF	303
78% OPC + 20% Type 2 NP + 2% SF	No initiation
77% OPC + 20% Type 2 NP + 3% SF	No initiation
76% OPC + 20% Type 2 NP + 4% SF	No initiation
75% OPC + 20% Type 2 NP + 5% SF	No initiation

Table 4-15: Time to initiation of reinforcement corrosion in Type 3 NP plus SF

Cementitious Materials	Time to Initiation of Corrosion Days
100% OPC	177
80% OPC + 20% Type 3 NP	234
79% OPC + 20% Type 3 NP + 1% SF	310
78% OPC + 20% Type 3 NP + 2% SF	No initiation
77% OPC + 20% Type 3 NP + 3% SF	No initiation
76% OPC + 20% Type 3 NP + 4% SF	No initiation
75% OPC + 20% Type 3 NP + 5% SF	No initiation

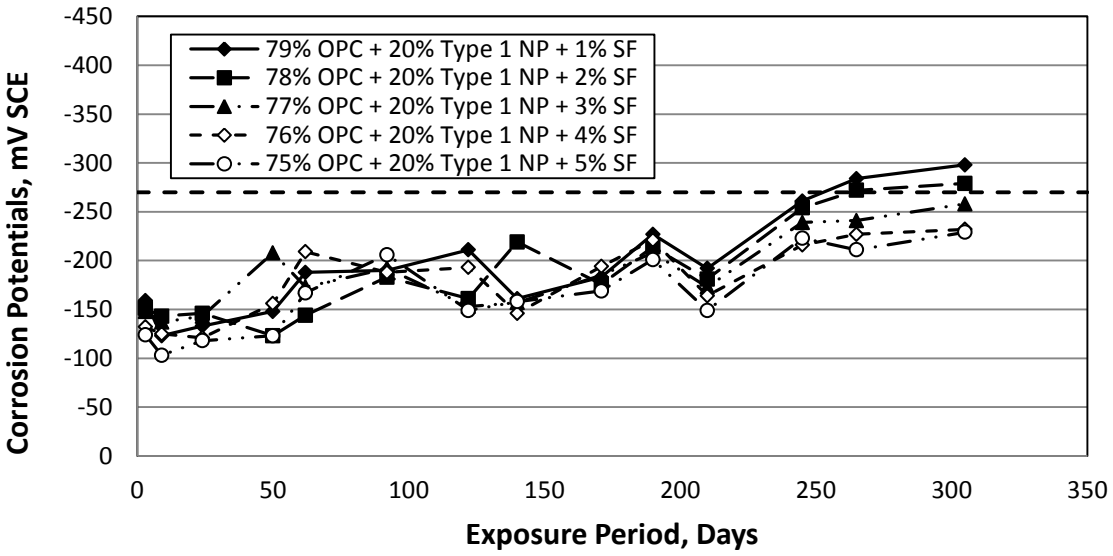

Figure 4-58: Corrosion potentials of steel in Type 1 NP concrete with varying SF

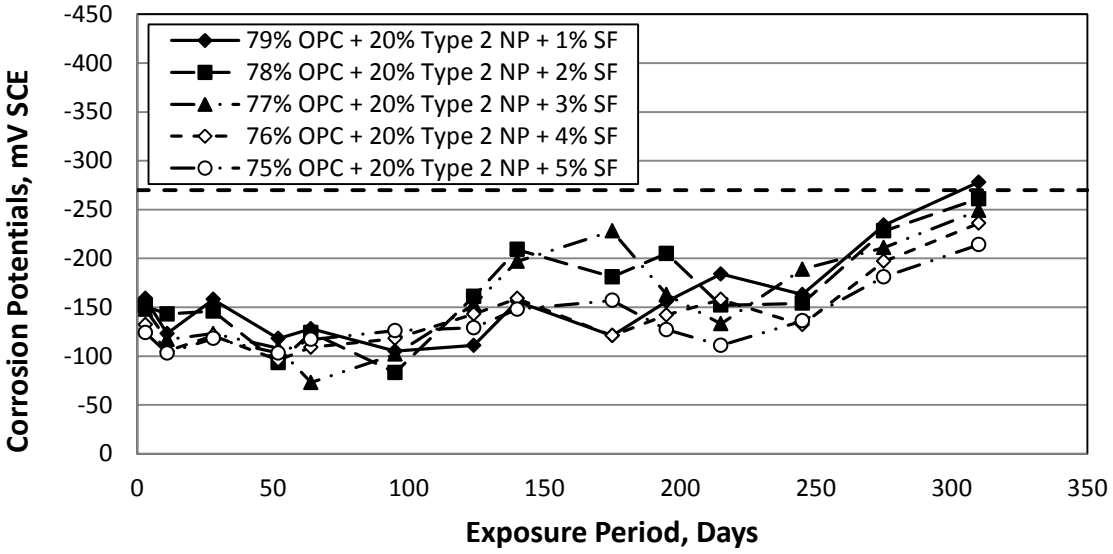

Figure 4-59: Corrosion potentials on steel in Type 2 NP concrete with varying SF

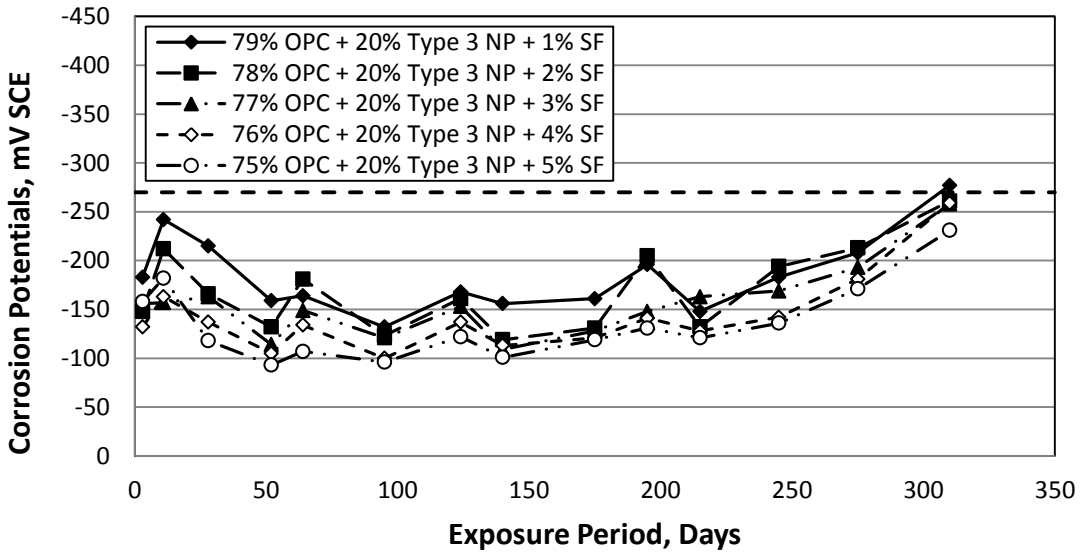

Figure 4-60: Corrosion potentials on steel in Type 3 NP concrete with varying SF

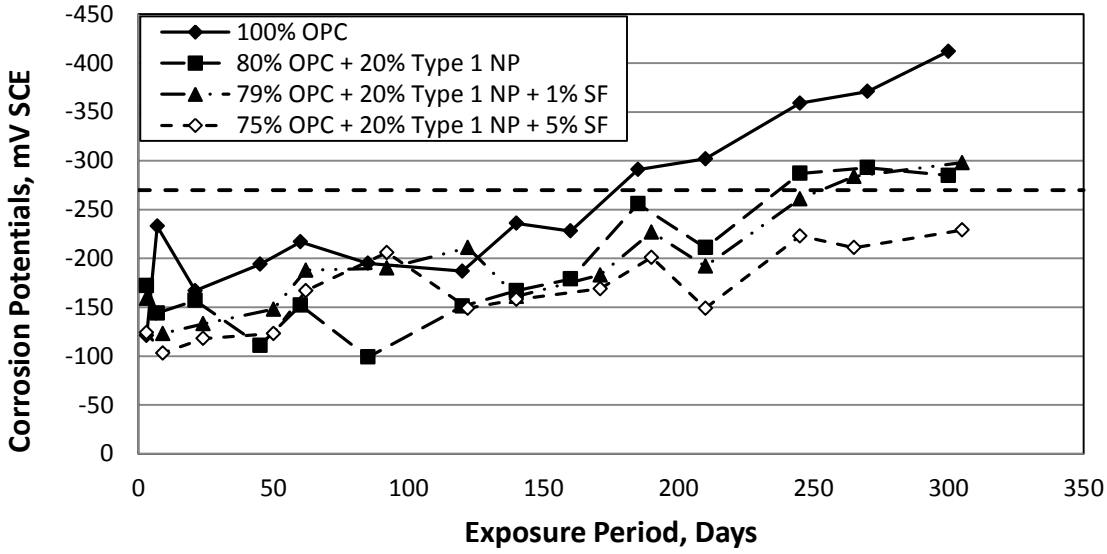

Figure 4-61: Comparison of corrosion potentials on steel in OPC and Type 1 NP plus SF

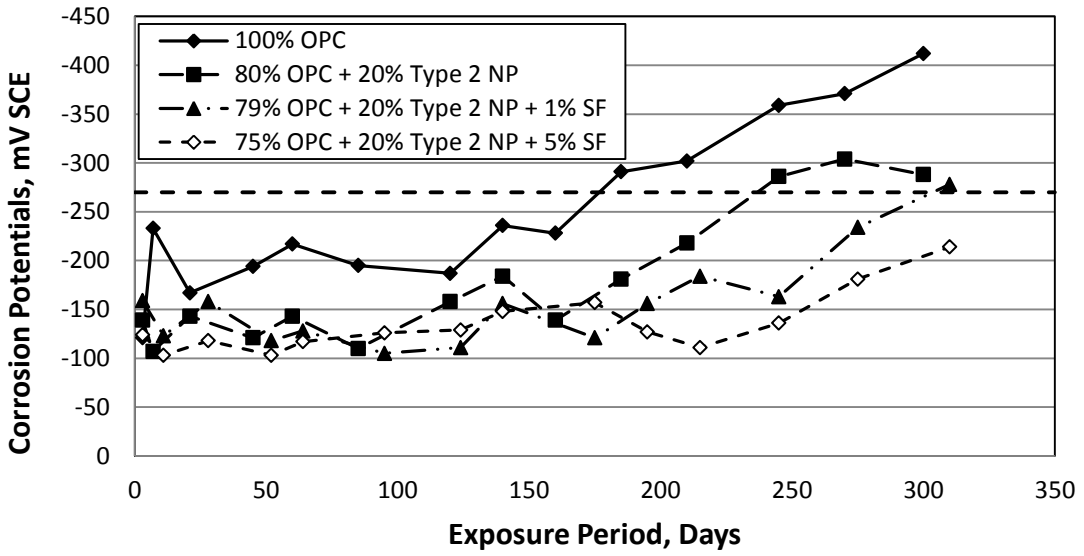

Figure 4-62: Comparison of corrosion potentials on steel in OPC and Type 2 NP plus SF

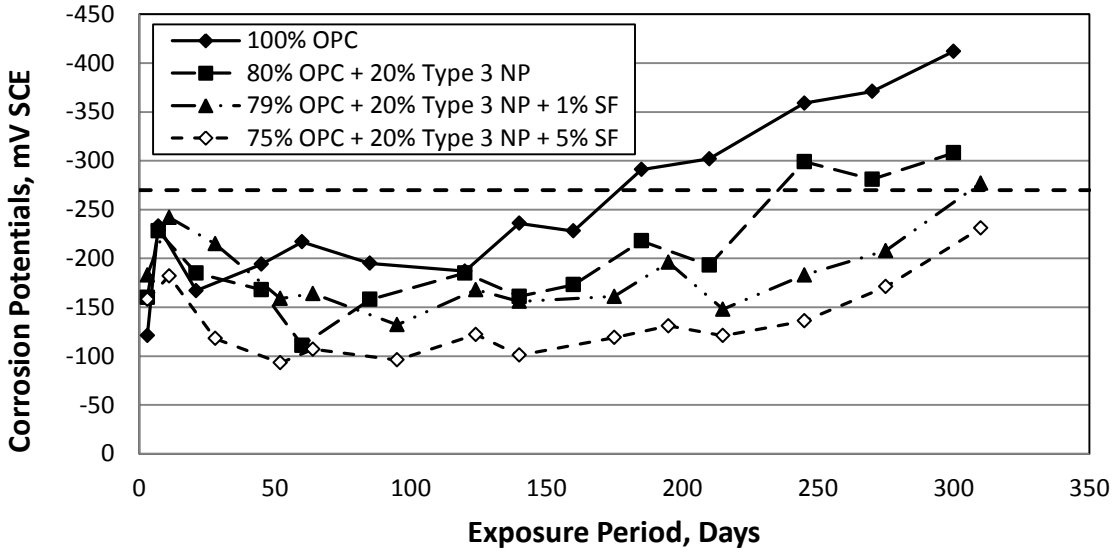

Figure 4-63: Comparison of corrosion potentials on steel in OPC and Type 3 NP plus SF

4.5.3 Effect of Chemical Activation of Natural Pozzolan Time to Initiation of Corrosion

Table 4-16 shows the time to corrosion initiation for the specimens prepared with the various 20% NPs (All three types) and 7% HL. As compared with the corrosion initiation time of both OPC and the specimens prepared with only 20% NP. Figures 4-64 through 4-66 show the corrosion potentials of these specimens. These figures were used to calculate the time to initiation of reinforcement corrosion. An improvement in the corrosion initiation time was noted. In fact, no initiation of corrosion was detected for all three types of NP with 7% HL, during the whole period of monitoring (up till 300 days). Lime when added with pozzolans increase the resistance of concrete towards the corrosion of reinforcement embedded in it [72].

Table 4-16: Time to initiation of corrosion on steel in OPC and NP plus HL

Cementitious Materials	Time to Initiation of Corrosion, Days
100% OPC	177
80% OPC + 20% Type 1 NP	237
80% OPC + 20% Type 2 NP	238
80% OPC + 20% Type 3 NP	234
73% OPC + 20% Type 1 NP + 7% HL	--
73% OPC + 20% Type 2 NP + 7% HL	--
73% OPC + 20% Type 3 NP + 7% HL	--

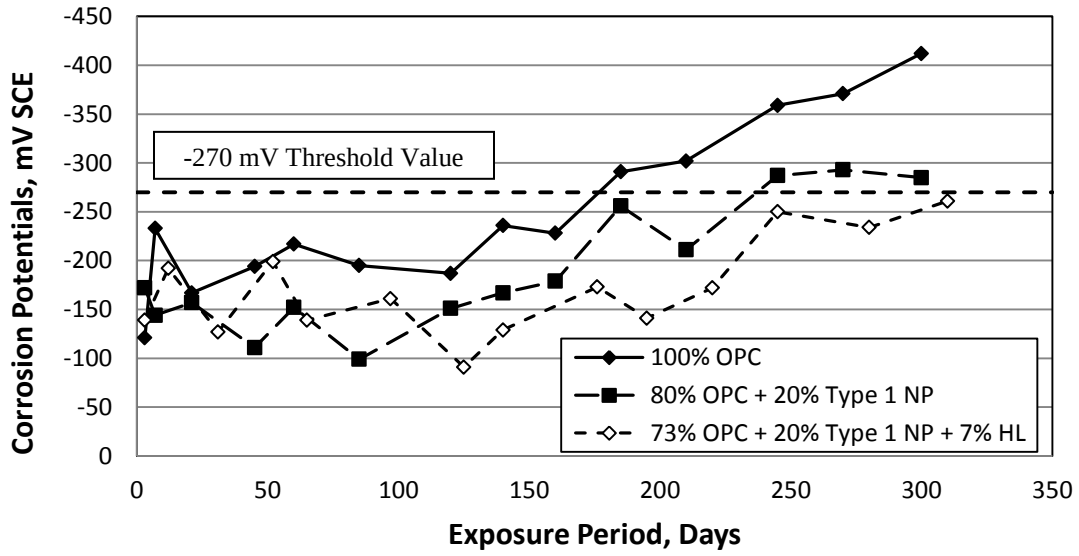

Figure 4-64: Corrosion potentials of steel in specimens with HL and Type 1 NP

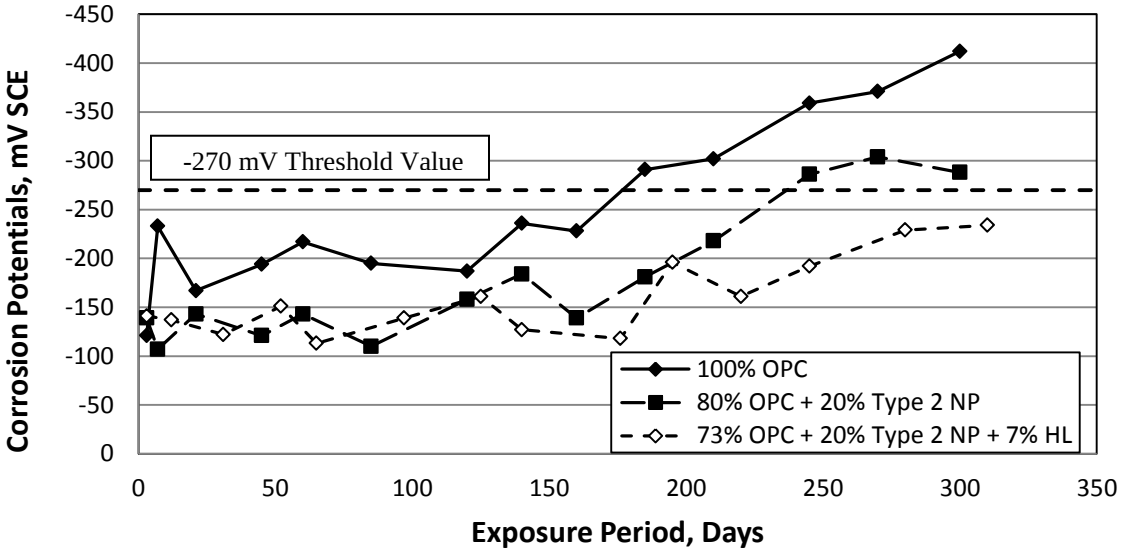

Figure 4-65: Corrosion potentials of steel in specimens with HL and Type 2 NP

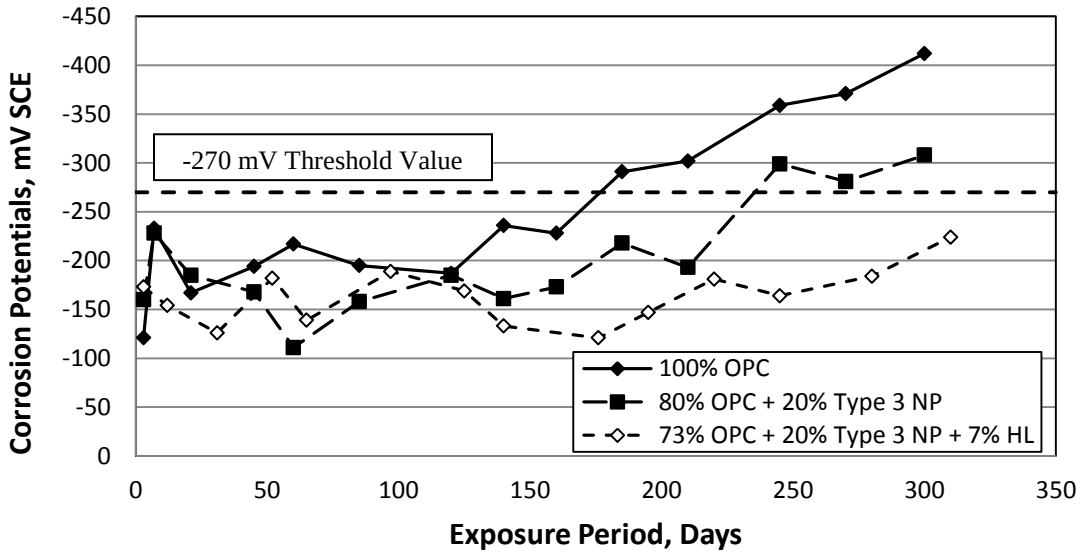

Figure 4-66: Corrosion potentials of steel in specimens with HL and Type 3 NP

4.5.4 Effect of Mechanical Activation of Natural Pozzolan on Time to initiation of Corrosion

Table 4-17 shows the time to initiation of reinforcement corrosion in the specimens prepared with 20% OPC replacement by finer NP. These times were obtained from Figures 4-67, 4-68 and 4-69 that show the corrosion potentials for the specimens prepared with finer Type 1, 2 and 3 NP, respectively, in comparison to the specimens with those in OPC and coarser NP. From the data in Table 4-17, it is seen that by increasing the fineness of NPs, the time to corrosion initiation increased for all the three types of NP. For finer NPs the time to initiation of corrosion was 286, 300 and 307 days compared to 237, 234 and 234 days for coarser NPs and 177 days in OPC. Increasing the fineness of pozzolanic materials increases the reactivity of pozzolan. This higher reactivity results in more secondary hydrated product making concrete dense, reducing the permeability of

moisture, oxygen and chloride ion in concrete which in turn decreases the reinforcement corrosion [46, 73].

Table 4-17: Time for initiation of reinforcement corrosion of OPC and NP

Cementitious Materials	Time to Initiation of Corrosion, Days
100% OPC	177
80% OPC + 20% Type 1 NP	237
80% OPC + 20% Type 2 NP	238
80% OPC + 20% Type 3 NP	234
80% OPC + 20% Type 1 NP (Fine)	286
80% OPC + 20% Type 2 NP (Fine)	300
80% OPC + 20% Type 3 NP (Fine)	307

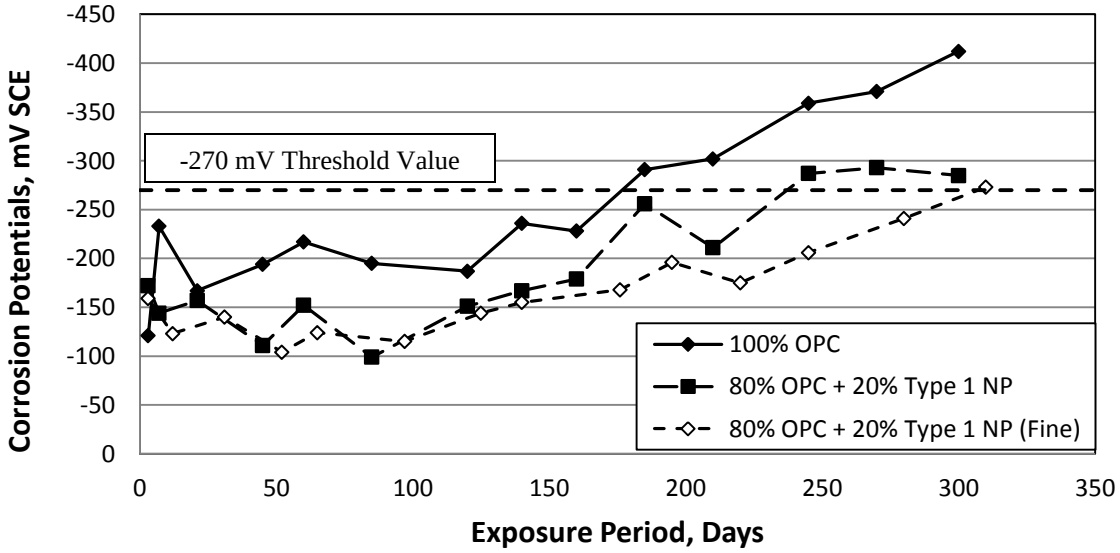

Figure 4-67: Corrosion potentials on steel in specimens of finer Type 1 NP

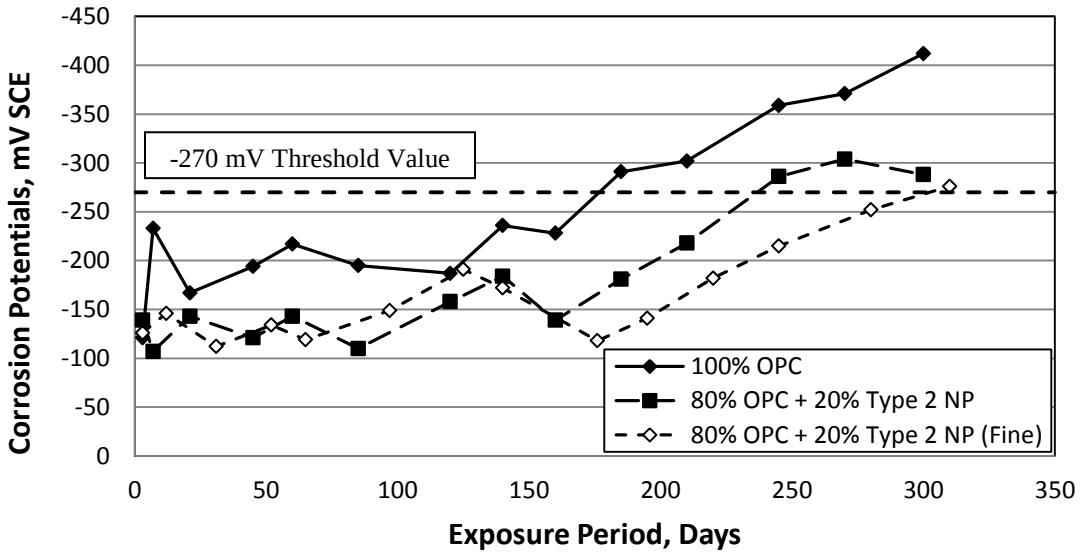

Figure 4-68: Corrosion potentials on steel in specimens of finer Type 2 NP

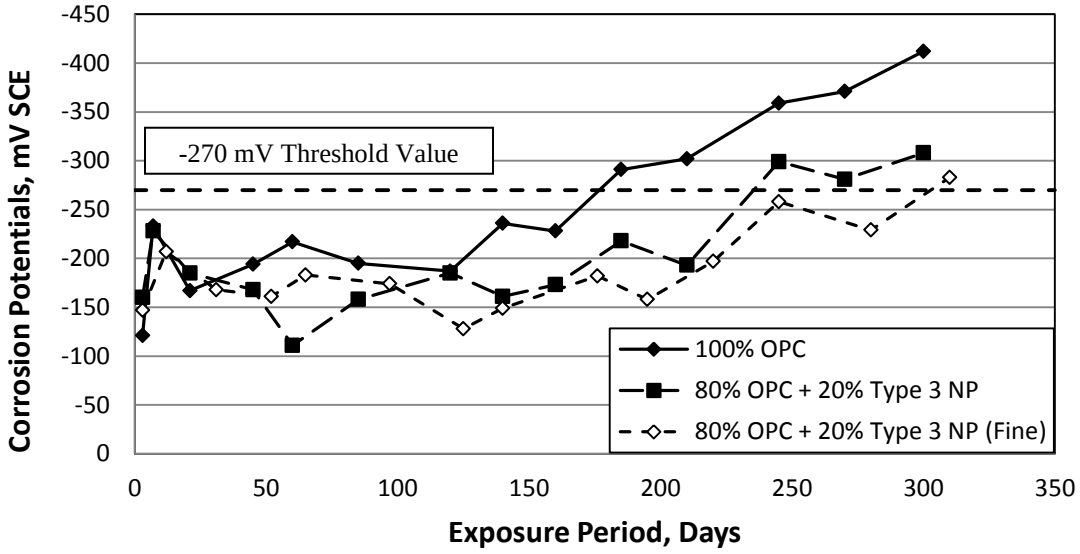

Figure 4-69: Corrosion potentials on steel in specimens of finer Type 3 NP

4.5.5 Time to Initiation of Corrosion in NP-Blended Cement

Table 4-18 shows data on the time to initiation of corrosion in both NP-blended cements concrete specimens compared with OPC concrete specimen. The use of NP-blended cements in place of OPC has increased the time to corrosion initiation. For both the blended cements, the time to corrosion initiation was 265 and 273 days compared to 177 days of OPC. The time to corrosion initiation in concrete specimens with NP added in lab was in the range of 230 days while in the NP-blended cements it was about 270 days. Figure 4-70 shows the corrosion potentials for above said specimens. As discussed in Section 4.4.5 the blended cements showed less chloride ingress in the specimens compared to OPC which resulted in less corrosion in the reinforcement embedded in blended cement concretes than that of OPC.

Table 4-18: Time to initiation of corrosion on steel in NP-blended cements

Cementitious Materials	Time to Initiation of Corrosion, Days
100% OPC	177
NP-blended Cement 1	265
NP-blended Cement 2	273

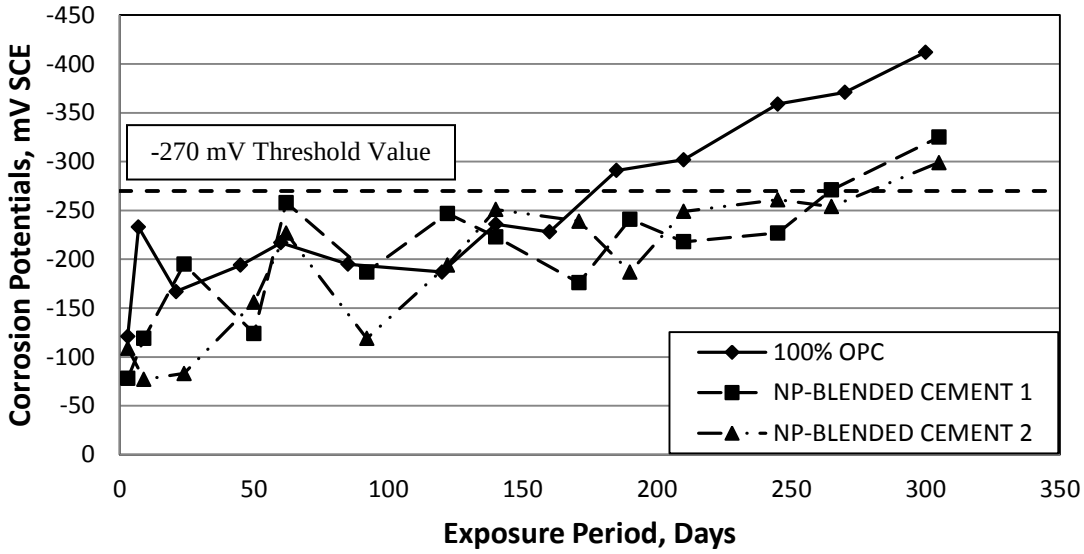

Figure 4-70: Corrosion potentials of steel in OPC and NP-blended cements

4.6 Corrosion Current Density

The corrosion current density (I_{corr}) was measured at different intervals on reinforced concrete specimens that were placed in 5% NaCl solution. These values are plotted in Figures 4-71 through 4-84. As expected, I_{corr} increased with an increase in the exposure period in all the specimens. I_{corr} for all the specimens at 300 days of exposure are summarized in Tables 4-19 through 4-29.

4.6.1 Effect of Natural Pozzolan Addition as a Partial Replacement of OPC on Corrosion Current Density

Figure 4-71 shows the corrosion current density of OPC and 20% NP concretes (all three types). The I_{corr} in OPC concrete was more than 0.3 $\mu A/cm^2$ after about 193 days while none of all the specimens prepared with 20% NP, as a partial replacement of OPC, crossed this threshold value even after 300 days. Table 4-19 summarizes the corrosion current density after 300 days for all the specimens discussed above. Najimi [19] and Fajardo [40] conducted linear polarization resistance test on reinforced concrete specimens prepared with the addition of natural pozzolan and reported that there is a significant improvement in the resistance to reinforcement corrosion as compared to OPC control mix. There is a good relation between the amount chloride ingress and resistance of concrete towards corrosion of reinforcement embedded in it [74]. As discussed in Section 4.4.1 addition of NP reduces the chloride diffusion into the concrete which make it more resistive to reinforcement corrosion. Hossain et al. found that that addition of volcanic ash showed better performance in terms of chloride diffusivity and at the same time increased the long term corrosion resistance, compared to OPC specimens [74].

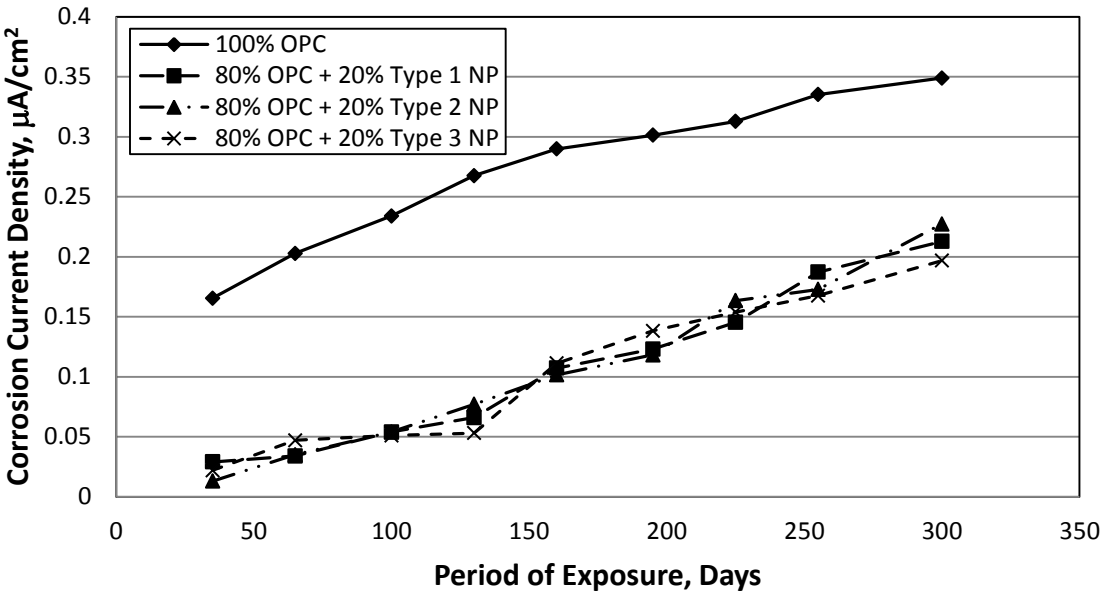

Figure 4-71: Corrosion current density on steel in OPC and NP concrete specimens

Table 4-19: Corrosion current density on steel in OPC and NP concrete specimens after 300 days

Cementitious Materials	Corrosion Current Density, µA/cm^2	Improvement Factor
100% OPC	0.349	-
80% OPC + 20% Type 1 NP	0.213	1.67
80% OPC + 20% Type 2 NP	0.227	1.54
80% OPC + 20% Type 3 NP	0.197	1.77

4.6.2 Effect of Physical Activation of Natural Pozzolan on Corrosion Current Density

Figures 4-72, 4-73 and 4-74 depict the data on the effect of adding SF in varying dosage (1 to 5%) to the 20% Type 1, 2 and 3 NPs, respectively. The corrosion current density

decreased with the increase in the amount of SF added to all the three types of NP. Tables 4-20, 4-21 and 4-22 summarize the corrosion current densities after an exposure period of 300 days for all the specimens prepared with SF. These values are also compared with the I_{corr} on the steel in 20% NP without SF and OPC.

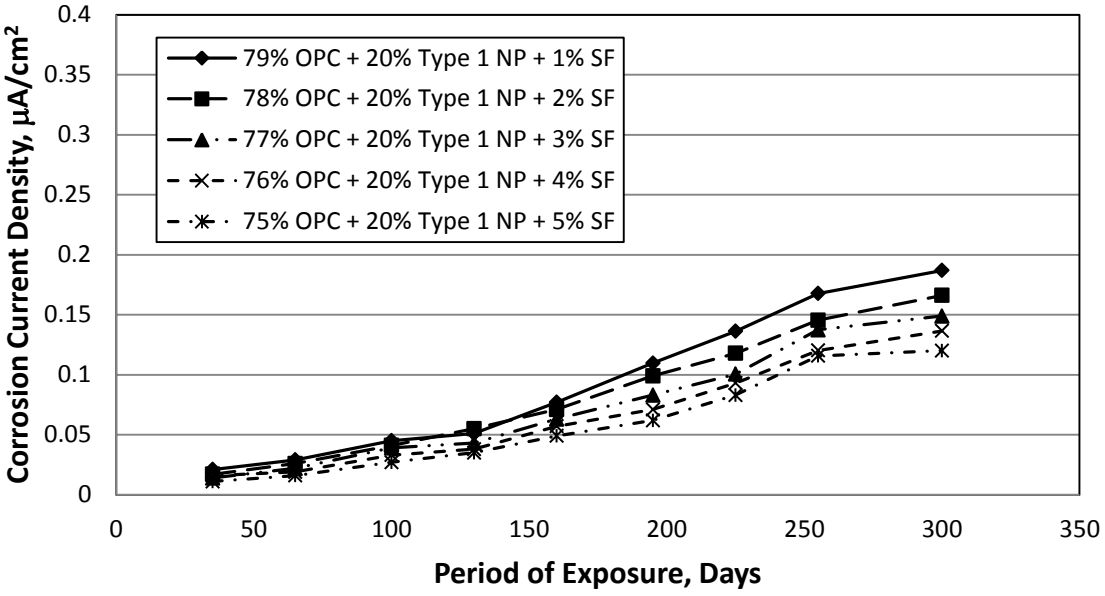

Figure 4-72: Corrosion current density on steel in OPC and Type 1 NP plus SF

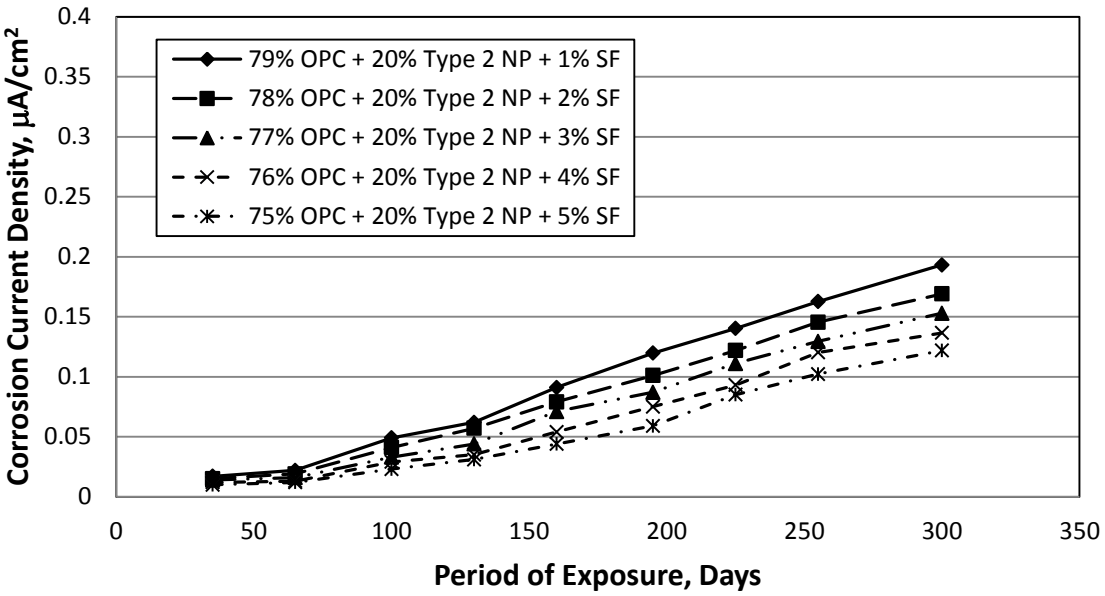

Figure 4-73: Corrosion current density on steel in OPC and Type 2 NP plus SF

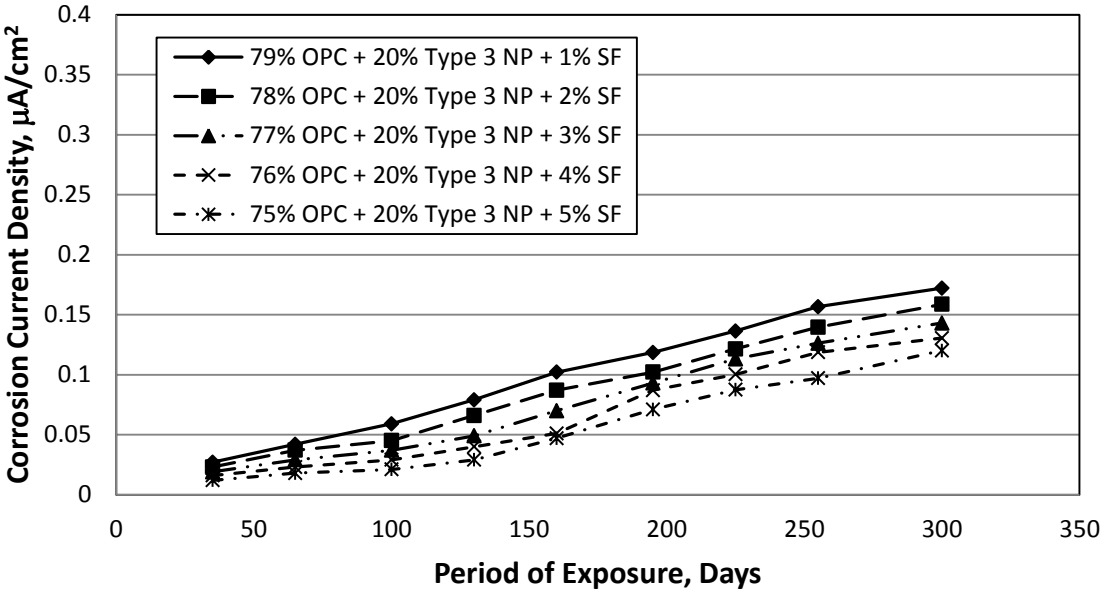

Figure 4-74: Corrosion current density on steel in OPC and Type 3 NP plus SF

Referring to Figures 4-72 to 4-74, it can be noted that the maximum corrosion current density was in 1% SF concrete, while 5% SF showed the lowest. This is true for all three

types of NP. Figures 4-75, 4-76 and 4-77 compare the corrosion current densities for OPC, 20% NP without SF and 20% NP with 1% and 5% SF. The data in Figure 4-75 show that the inclusion of 1% SF in 20% Type 1 NP decreased the corrosion current density. After 300 days of exposure, the I_{corr} noted was 0.187 μA/cm^2 compared to 0.349 μA/cm^2 for OPC specimens. However, the minimum I_{corr} after 300 days of exposure was noted in 5% SF cement concrete, which was 0.12 μA/cm^2. This trend is also true for Type 2 and 3 NP, as shown in Figure 4-76 and 4-77. As Discussed in Section 4.4.2 that with the increase in SF content the chloride diffusion in the concrete decreases, which increases the resistant of concrete to reinforcement corrosion. This trend is also verified with the corrosion potentials which also show that the potentials dropped as the SF content increased.

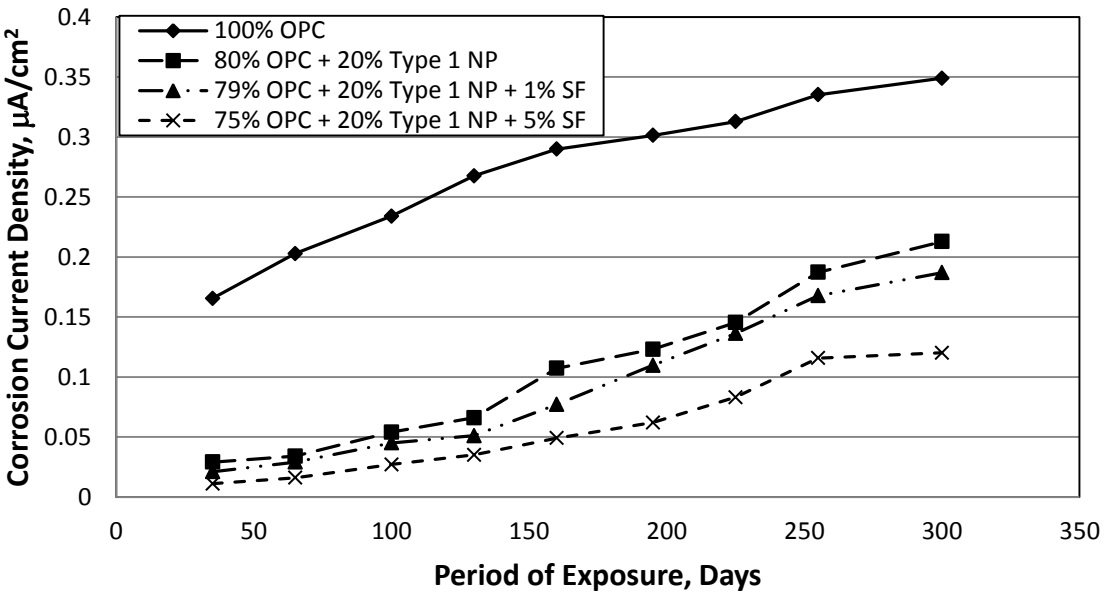

Figure 4-75: Comparison of corrosion current density on steel in OPC and Type 1 NP plus SF

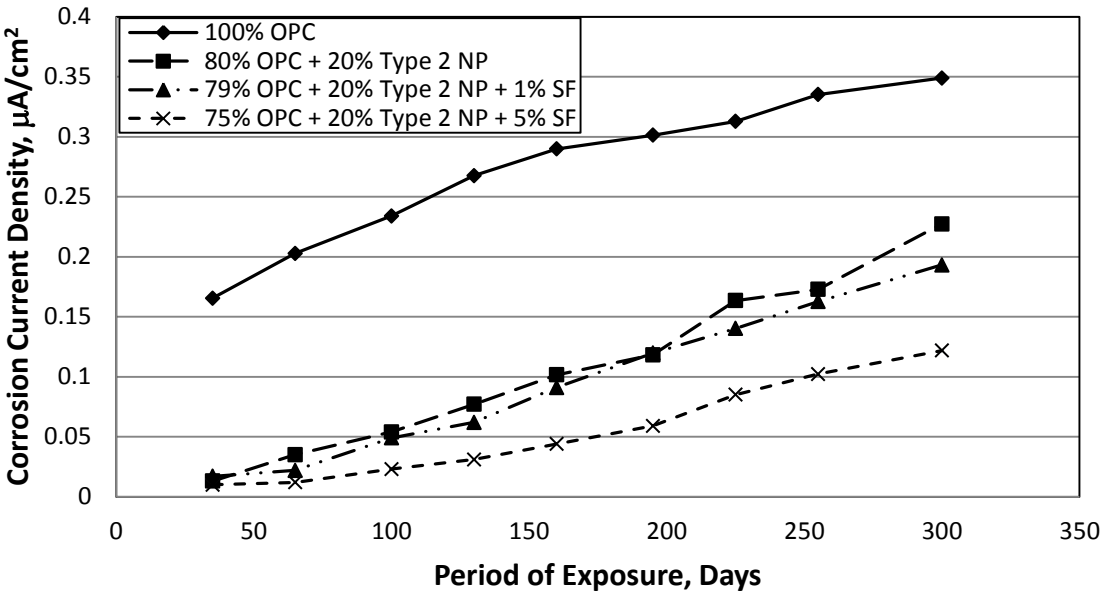

Figure 4-76: Comparison of corrosion current density on steel in OPC and Type 2 NP plus SF

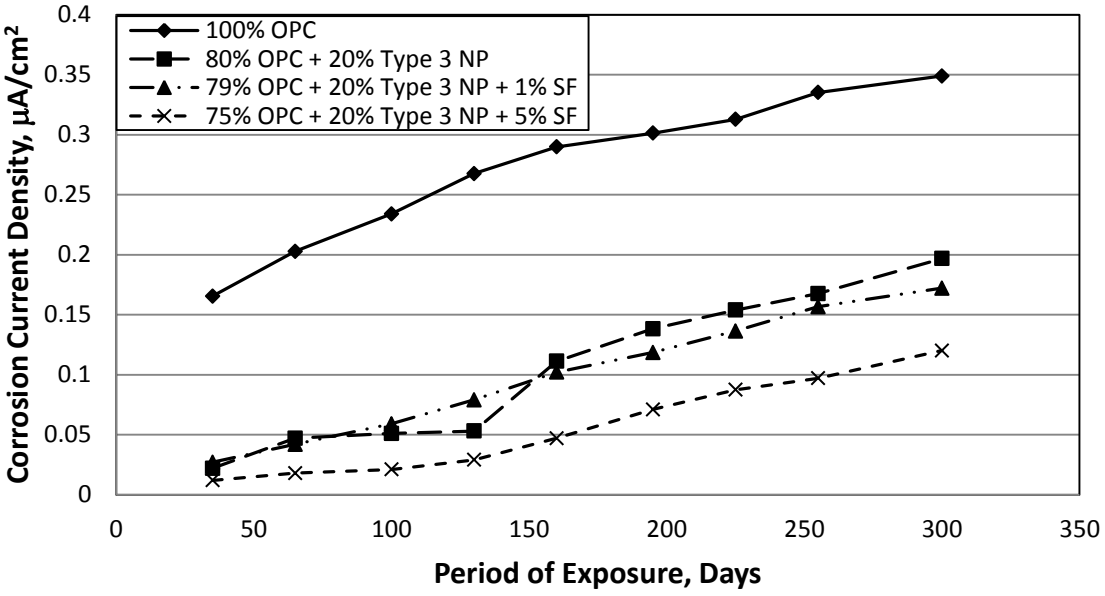

Figure 4-77: Comparison of corrosion current density on steel in OPC and Type 3 NP plus SF

Table 4-20: Corrosion current density on steel in OPC and Type 1 NP specimens with SF

Cementitious Materials	Corrosion Current Density, µA/cm^2 *	Improvement Factor
100% OPC	0.349	-
80% OPC + 20% Type 1 NP	0.213	1.67
79% OPC + 20% Type 1 NP + 1% SF	0.187	1.87
78% OPC + 20% Type 1 NP + 2% SF	0.166	2.10
77% OPC + 20% Type 1 NP + 3% SF	0.149	2.34
76% OPC + 20% Type 1 NP + 4% SF	0.137	2.55
75% OPC + 20% Type 1 NP + 5% SF	0.120	2.91

* After 300 days of exposure

Table 4-21: Corrosion current density on steel in OPC and Type 2 NP specimens with SF

Cementitious Materials	Corrosion Current Density, µA/cm^2 *	Improvement Factor
100% OPC	0.349	-
80% OPC + 20% Type 2 NP	0.227	1.54
79% OPC + 20% Type 2 NP + 1% SF	0.193	1.81
78% OPC + 20% Type 2 NP + 2% SF	0.169	2.07
77% OPC + 20% Type 2 NP + 3% SF	0.153	2.28
76% OPC + 20% Type 2 NP + 4% SF	0.137	2.55
75% OPC + 20% Type 2 NP + 5% SF	0.122	2.86

* After 300 days of exposure

Table 4-22: Corrosion current density on steel in OPC and Type 3 NP specimens with SF

Cementitious Materials	Corrosion Current Density, µA/cm^2 *	Improvement Factor
100% OPC	0.349	-
80% OPC + 20% Type 3 NP	0.197	1.77
79% OPC + 20% Type 3 NP + 1% SF	0.172	2.03
78% OPC + 20% Type 3 NP + 2% SF	0.159	2.19
77% OPC + 20% Type 3 NP + 3% SF	0.143	2.44
76% OPC + 20% Type 3 NP + 4% SF	0.131	2.66
75% OPC + 20% Type 3 NP + 5% SF	0.120	2.91

* After 300 days of exposure

4.6.3 Effect of Chemical Activation of Natural Pozzolan on Corrosion Current Density

Figure 4-78 shows the corrosion current density on steel specimen prepared with 20% Type 1 NP and 7% HL, in comparison to OPC and 20% Type 1 NP without HL. OPC specimens showed higher corrosion current density from the beginning. At the initial period, the specimens with HL showed a bit higher values of corrosion current density than that of NP. However, at 120 days, the trend was reversed and the specimens without HL continued to show higher corrosion current density than specimens with HL.

For Type 2 NP, the specimens with HL showed higher corrosion current density compared to that of NP specimen without HL till 100 days. Thereafter, the specimens with HL showed lower corrosion current density, as shown in Figure 4-79. This trend is also true for Type 3 NP, as shown in Figure 4-80 with the point at which the corrosion current density of specimen prepared with HL starts to drop lies at 150 days. Tables 4-23,

4-24 and 4-25 summarize the corrosion current density of above discussed specimens. It is also seen in Section 4.5.3 that at initial period of exposure the corrosion potentials for specimens with HL were higher than that of NP specimens prepared without HL. However, the corrosion potentials dropped down at later period of exposure.

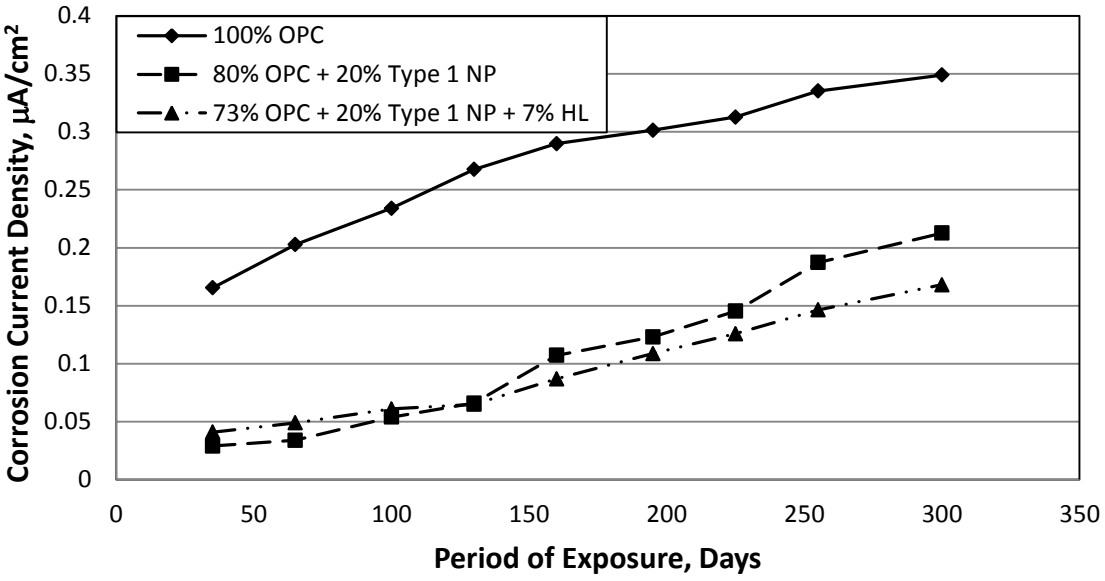

Figure 4-78: Corrosion current density on steel in specimens with HL and Type 1 NP

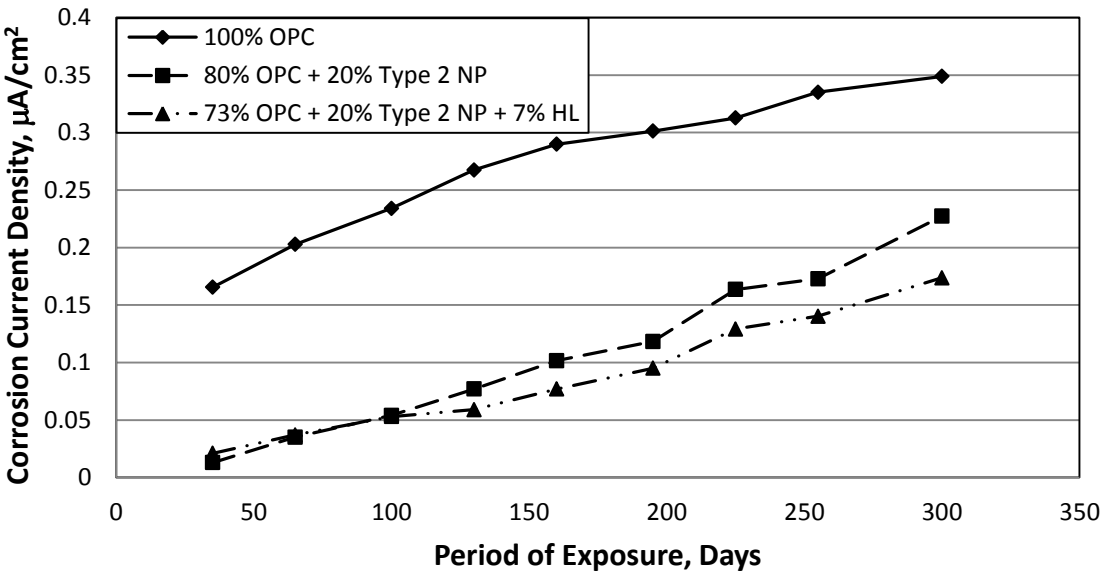

Figure 4-79: Corrosion current density on steel in specimens with HL and Type 2 NP

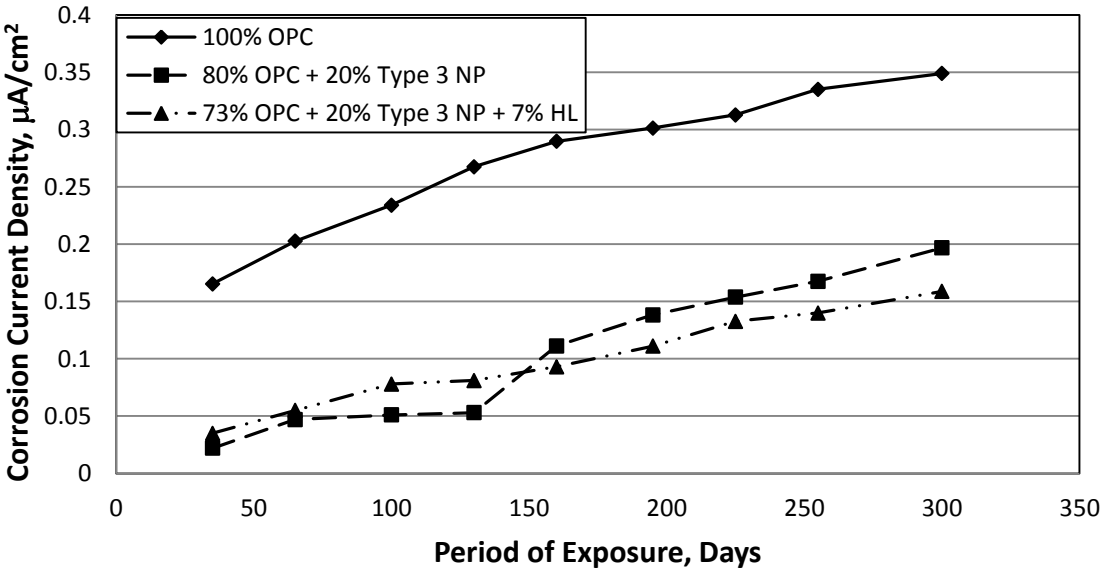

Figure 4-80: Corrosion current density on steel in specimens with HL and Type 3 NP

Table 4-23: Corrosion current density on steel in OPC and Type 1 NP plus HL after 300 days of exposure

Cementitious Materials	Corrosion Current Density, µA/cm^2	Improvement Factor
100% OPC	0.349	-
80% OPC + 20%Type 1 NP	0.213	1.67
73% OPC + 20%Type 1 NP + 7% HL	0.168	2.08

Table 4-24: Corrosion current density on steel in OPC and Type 2 NP plus HL after 300 days of exposure

Cementitious Materials	Corrosion Current Density, µA/cm^2	Improvement Factor
100% OPC	0.349	-
80% OPC + 20%Type 2 NP	0.227	1.58
73% OPC + 20%Type 2 NP + 7% HL	0.174	2.01

Table 4-25: Corrosion current density on steel in OPC and Type 3 NP plus HL after 300 days of exposure

Cementitious Materials	Corrosion Current Density, µA/cm^2	Improvement Factor
100% OPC	0.349	-
80% OPC + 20% TYPE 3 NP	0.197	1.77
73% OPC + 20% TYPE 3 NP + 7% HL	0.159	2.19

4.6.4 Effect of Mechanical Activation of Natural Pozzolan on Corrosion Current Density

Figures 4-81, 4-82 and 4-83 depict I_{corr} on steel in the specimens prepared with both the fineness of Type 1, 2 and 3 NPs, respectively. For all three types of NPs, the fineness did not have a major effect in decreasing the corrosion current density. After 300 days of exposure the corrosion current density in finer NPs specimens were 0.201, 0.197 and 0.173 µA/cm^2, compared to 0.213, 0.227 and 0.197 µA/cm^2 of coarser NPs. However, at all the exposure periods, the corrosion current density of finer NP was less than that of coarser one for all types of NP, but the difference was not that significant. Tables 4-26, 4-27 and 4-28 summarize the corrosion current densities after 300 days of exposure to the 5% NaCl for the above discussed specimens.

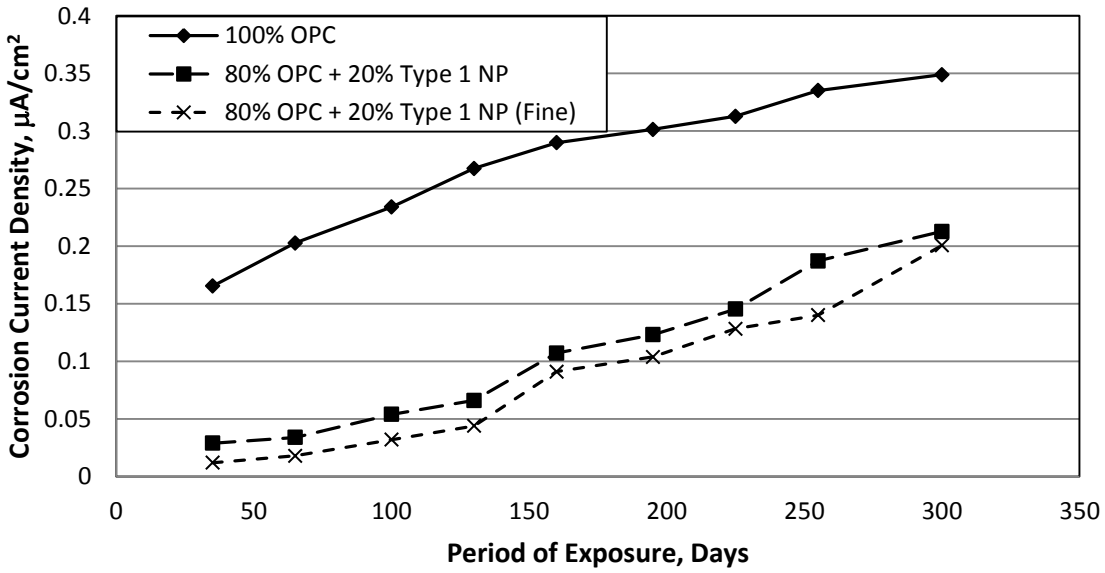

Figure 4-81: Effect of fineness of Type 1 NP on I_{corr}

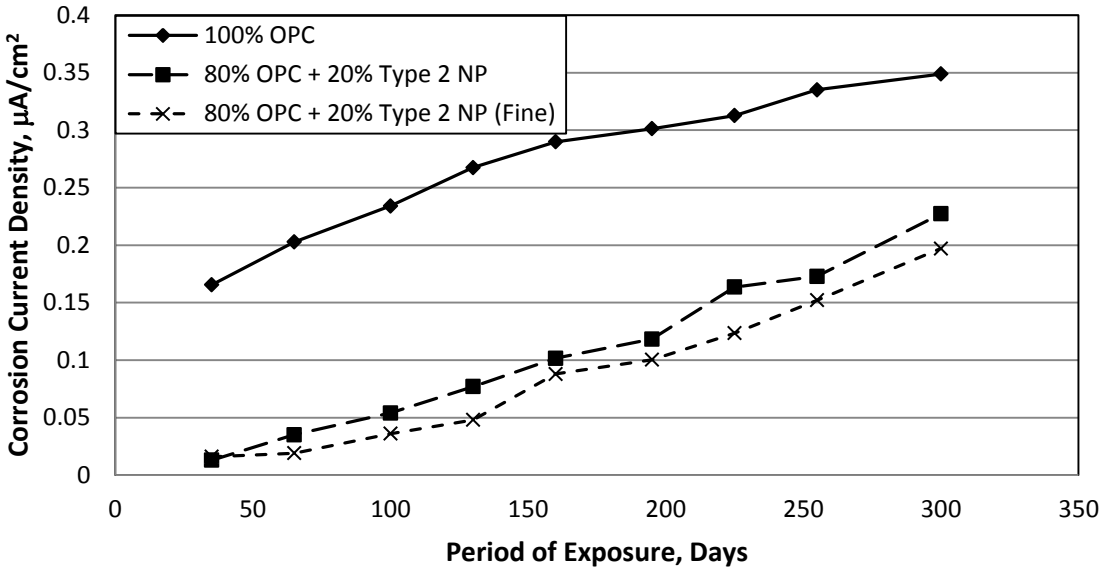

Figure 4-82: Effect of fineness of Type 2 NP on I_{corr}

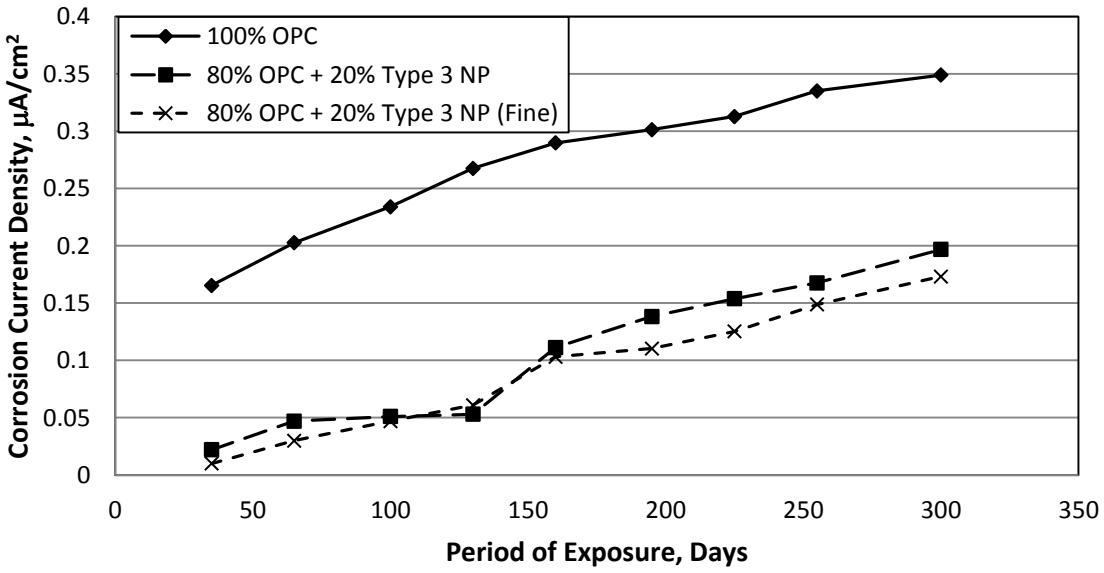

Figure 4-83: Effect of fineness of Type 3 NP on I_{corr}

Table 4-26: Corrosion current density on steel in finer Type 1 NP concrete after 300 days of exposure

Cementitious Materials	Corrosion Current Density, µA/cm^2	Improvement Factor
100% OPC	0.349	-
80% OPC + 20%Type 1 NP	0.213	1.64
80% OPC + 20%Type 1 NP (Fine)	0.201	1.74

Table 4-27: Corrosion current density on steel in finer Type 2 NP concrete after 300 days of exposure

Cementitious Materials	Corrosion Current Density, µA/cm^2	Improvement Factor
100% OPC	0.349	-
80% OPC + 20%Type 2 NP	0.227	1.54
80% OPC + 20%Type 2 NP (Fine)	0.197	1.77

Table 4-28: Corrosion current density on steel in finer Type 3 NP concrete after 300 days of exposure

Cementitious Materials	Corrosion Current Density, µA/cm^2	Improvement Factor
100% OPC	0.349	-
80% OPC + 20% TYPE 3 NP	0.197	1.77
80% OPC + 20% TYPE 3 NP (Fine)	0.173	2.02

4.6.5 Corrosion Current Density of NP-Blended Cement

As shown in Figure 4-84, the I_{corr} in both the NP-blended cement concretes was lower than that on the steel in OPC concrete. The I_{corr} in the OPC was 0.35 µA/cm^2 while it was

around 0.26 μA/cm^2 in the blended cement concretes. As discussed in Sections 4.5.1 through 4.5.6 that use of pozzolanic material and blended cements increase the resistance of concrete to reinforcement corrosion. The data presented in this figure clearly depicts better performance of blended cements compared to OPC. Table 4-29 summarizes the corrosion current density at 300 days for both NP-Blended cement concretes. In Figure 4-84 it

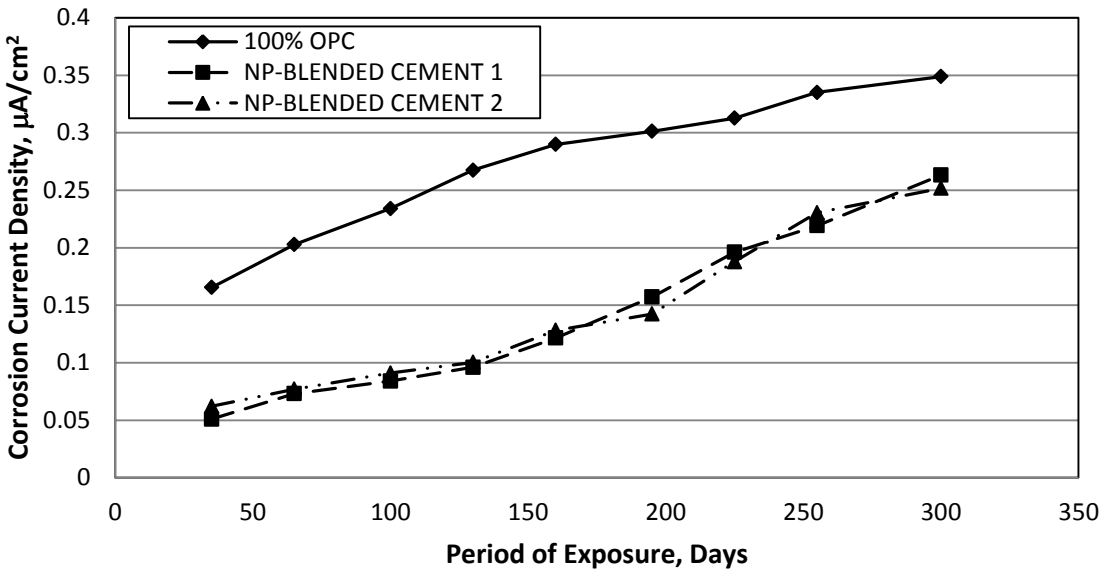

Figure 4-84: Corrosion current density on steel in NP-blended cements

Table 4-29: Corrosion current density on steel in NP-blended cements after 300 days

Cementitious Materials	Corrosion Current Density, μA/cm^2	Improvement Factor
100% OPC	0.349	-
NP-BLENDED CEMENT 1	0.263	1.33
NP-BLENDED CEMENT 2	0.252	1.39

4.7 Resistance to Sulfate Attack

Specimens prepared from all types of concrete, under study, were exposed to 5% sulfate solution. After 12 months of exposure to sulfate solution, the specimens were taken out and visually examined for surface deterioration and tested for their residual compressive strength. The compressive strength of the specimens exposed to sulfate solution was compared with the strength of specimens exposed to water.

Addition of pozzolanic material in concrete as a partial replacement of OPC affects the performance of concrete, when exposed to sulfate environment. Literature shows that this effect may be incremental in resistance to sulfate attack or, in other cases; the addition of pozzolanic material may decrease the resistance to sulfate attack. Ghrici [16] studied binary mixes of OPC-NP and ternary mixes of OPC-NP-limestone filler and reported that the addition of 30% natural pozzolan showed half as much expansion as in OPC, and the addition of 15% limestone filler did not improve the sulfate attack resistance of mix. Colak [22] used natural pozzolan as a partial replacement of OPC in different amounts and reported that using NP, in all cases, decreased the resistance to sulfate attack. This is because of the inclusion of natural pozzolans made the specimens denser than that of OPC. Rodriguez and Uribe [34] reported that mixes prepared with NP performed even better than sulfate resistant Type V cement. Kilinckale [35] studied the strength loss of mortars prepared with different dosages of natural pozzolan when exposed to sulfate environment, and reported that mixes with natural pozzolan showed higher durability than OPC. Hossain and Lachemi [36] studied the weight loss due to sulfate attack, in specimens prepared with natural pozzolan and reported that initially there was a weight

gain in all specimens. Up to 18 months of exposure, the specimens prepared with natural pozzolans performed almost equal to OPC but after 18 months of exposure, the specimens of OPC performed better than all natural pozzolan specimens and showed higher weight loss. Al-Amoudi [53] reported that blended cements exposed to magnesium sulfate environment showed higher strength loss than OPC but on exposure to sodium sulfate showed less weight loss and expansion than OPC.

4.7.1 Visual Examination

Figures 4-85 through 4-91 show some of the specimens that were exposed to the sulfate solution after an exposure period of 12 months. In Figure 4-85, OPC specimens are shown after 6 and 12 months of exposure. Signs of sulfate deterioration were already visible at 6 months of exposure. This deterioration increased with 12 months of exposure.

Figure 4-86 shows the specimens prepared with 20% Type 1 NP after 6 and 12 months of exposure. No signs of deterioration were noted, even after 12 months of exposure. Similarly, no deterioration was noted on the surface of Type 2 and 3 NPs specimens. Similarly, no surface deterioration was noted on the specimens of NP-blended cement concrete, after 6 and 12 months of exposure, as shown in Figure 4-87.

Figures 4-88 and 4-89 depict the specimens prepared with 1 and 5% SF added to 20% Type 1 NP, after 6 and 12 months of exposure. Specimens with 5% SF exhibited no signs of surface deterioration even after 12 months. However, the specimens with 1% SF showed some signs of surface deterioration after 12 months of exposure, as shown in Figure 4-88.

Figure 4-90 shows the specimens prepared with 20% NP and 7% HL. Unlike all the previous cases, these specimens started to show signs of surface deterioration after 6 months of exposure. These specimens showed more deterioration than all the other specimens after 12 months of exposure, with surface softening at the corners, indicating there inferior performance in sulfate exposure as compared with all the other mixtures.

Figure 4-91 shows the specimens prepared with finer NP used as a 20% replacement of OPC. There were no signs of deterioration on the surface even after 12 months of exposure. Table 4-30 summarizes the visual observations made on specimens after 6 and 12 months of exposure to the sulfate solution.

Figure 4-85: OPC specimens after 6 and 12 months of exposure to sulfate solution

Figure 4-86: Specimens prepared with 20% NP after 6 and 12 months of exposure to sulfate solution

Figure 4-87: NP-blended cement specimens after 6 and 12 months of exposure to sulfate solution

Figure 4-88: 20% NP specimens with 1% SF after 6 and 12 months of exposure to sulfate solution

Figure 4-89: 20% NP specimens with 5% SF after 6 and 12 months of exposure to sulfate solution

Figure 4-90: 20% NP specimens with 7% HL after 6 and 12 months of exposure to sulfate solution

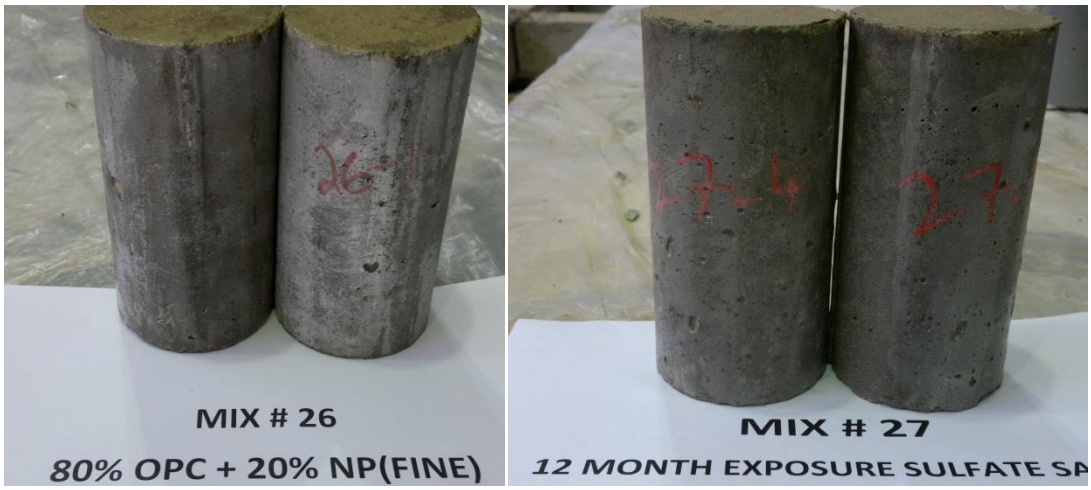

Figure 4-91: 20% NP specimens with increased fineness after 6 and 12 months of exposure to sulfate solution

Table 4-30: Visual observations on concrete specimens

Cementing Blend	Observation	
	6 month Exposure	12 Month Exposure
100% OPC	Surface Marking	Surface Marking
80% OPC + 20% Type 1 NP	No Deterioration	No Deterioration
80% OPC + 20% Type 2 NP	No Deterioration	No Deterioration
80% OPC + 20% type 3 NP	No Deterioration	No Deterioration
NP-blended Cement 1	No Deterioration	No Deterioration
NP-blended Cement 2	No Deterioration	No Deterioration
79% OPC + 20% Type 1 NP + 1% SF	No Deterioration	Surface Marking
78% OPC + 20% Type 1 NP + 2% SF	No Deterioration	No Deterioration
77% OPC + 20% Type 1 NP + 3% SF	No Deterioration	No Deterioration
76% OPC + 20% Type 1 NP + 4% SF	No Deterioration	No Deterioration
75% OPC + 20% Type 1 NP + 5% SF	No Deterioration	No Deterioration
79% OPC + 20% Type 2 NP + 1% SF	No Deterioration	Surface Marking
78% OPC + 20% Type 2 NP + 2% SF	No Deterioration	No Deterioration
77% OPC + 20% Type 2 NP + 3% SF	No Deterioration	No Deterioration
76% OPC + 20% Type 2 NP + 4% SF	No Deterioration	No Deterioration
75% OPC + 20% Type 2 NP + 5% SF	No Deterioration	No Deterioration
79% OPC + 20% Type 3 NP + 1% SF	No Deterioration	No Deterioration
78% OPC + 20% Type 3 NP + 2% SF	No Deterioration	No Deterioration
77% OPC + 20% Type 3 NP + 3% SF	No Deterioration	No Deterioration
76% OPC + 20% Type 3 NP + 4% SF	No Deterioration	No Deterioration
75% OPC + 20% Type 3 NP + 5% SF	No Deterioration	No Deterioration
73% OPC + 20% Type 1 NP + 7% HL	Surface Marking	Softening and spalling at corners
73% OPC + 20% Type 2 NP + 7% HL	Surface Marking	Softening and spalling at corners
73% OPC + 20% Type 3 NP + 7% HL	Surface Marking	Softening and spalling at corners
80% OPC + 20% Type 1 NP (Fine)	No Deterioration	No Deterioration
80% OPC + 20% Type 2 NP (Fine)	No Deterioration	No Deterioration
80% OPC + 20% Type 3 NP (Fine)	No Deterioration	No Deterioration

4.7.2 Effect of Natural Pozzolan Addition as a Partial Replacement of OPC on Sulfate Attack

Table 4-30 summarizes the strength loss of specimens exposed to sulfate for 12 months. For all three types of NP the strength loss is less than that of OPC. Figure 4-92 presents the graphical representation of the data in Table 4-30. The loss in strength of OPC was 4% while it was in a range of 1.7 to 2.1% in the NP cement concrete.

Table 4-31: Compressive strength loss of specimens prepared with OPC and 20% NP

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Sulfate Solution	
100% OPC	73.48	70.52	4.03%
80% OPC + 20% Type 1 NP	71.86	70.61	1.74%
80% OPC + 20% Type 2 NP	72.44	70.92	2.10%
80% OPC + 20% Type 3 NP	71.04	69.85	1.68%

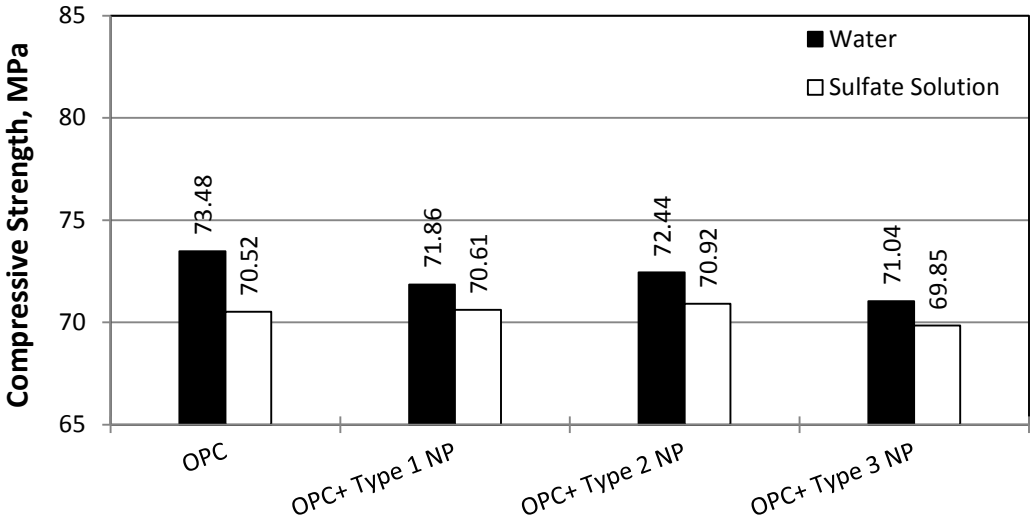

Figure 4-92: Compressive strength of OPC and NP specimens placed in water and sulfate solution for 12 months

4.7.3 Effect of Physical Activation of Natural Pozzolan Sulfate Attack

Silica fume was added in varying dosages (1 to 5%) to the concrete mixture with 20% NP as a recipe of physical activation. With the addition of SF, the resistance of concrete to sulfate attack increased. Just by adding 1% SF to any type of NP used in this study, an improvement was noted, with less strength loss been noted at the end of 12 month exposure period, as compared with other specimens with 20% NP without SF. Also, the specimens with 5% SF added to 20% NP, exhibited negligible strength loss. Tables 4-32 through 4-34 summarize the strength loss data for all the specimens prepared with the addition of SF to Type 1, 2 and 3 NPs, respectively. Figures 4-93 to 4-95 show the graphical representation of the data in Tables 4-32 through 4-34. The strength loss of OPC specimens was 4% while it was in the range of 2 to 0.1% in the specimens with SF.

Addition of silica fume reduces the permeability and improve the resistance of concrete to sulfate attack [66].

Table 4-32: Compressive strength loss in OPC and Type 1 NP plus SF

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Sulfate Solution	
100% OPC	73.48	70.52	4.03%
80% OPC + 20% Type 1 NP	71.86	70.61	1.74%
79% OPC + 20% Type 1 NP + 1% SF	74.12	72.97	1.55%
78% OPC + 20% Type 1 NP + 2% SF	74.83	73.98	1.14%
77% OPC + 20% Type 1 NP + 3% SF	76.06	75.55	0.67%
76% OPC + 20% Type 1 NP + 4% SF	77.31	76.96	0.45%
75% OPC + 20% Type 1 NP + 5% SF	78.21	78.06	0.19%

Table 4-33: Compressive strength loss in OPC and Type 2 NP plus SF

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Sulfate Solution	
100% OPC	73.48	70.52	4.03%
80% OPC + 20% Type 2 NP	72.44	70.92	2.10%
79% OPC + 20% Type 2 NP + 1% SF	74.96	73.68	1.71%
78% OPC + 20% Type 2 NP + 2% SF	75.12	74.17	1.26%
77% OPC + 20% Type 2 NP + 3% SF	76.81	76.34	0.61%
76% OPC + 20% Type 2 NP + 4% SF	77.54	77.25	0.37%
75% OPC + 20% Type 2 NP + 5% SF	79.12	79.01	0.14%

Table 4-34: Compressive strength loss in OPC and Type 3 NP plus SF

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Sulfate Solution	
100% OPC	73.48	70.52	4.03%
80% OPC + 20% Type 3 NP	71.04	69.85	1.68%
79% OPC + 20% Type 3 NP + 1% SF	75.03	74.05	1.31%
78% OPC + 20% Type 3 NP + 2% SF	76.63	75.85	1.02%
77% OPC + 20% Type 3 NP + 3% SF	78.15	77.63	0.67%
76% OPC + 20% Type 3 NP + 4% SF	78.90	78.64	0.33%
75% OPC + 20% Type 3 NP + 5% SF	79.78	79.64	0.17%

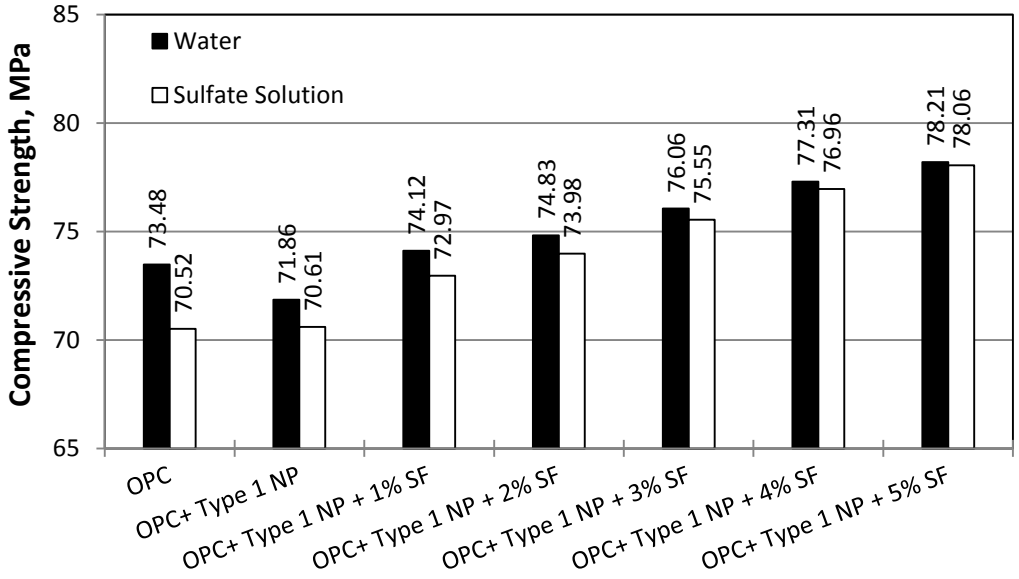

Figure 4-93: Compressive strength of OPC and Type 1 NP with varying SF placed in water and sulfate solution for 12 months

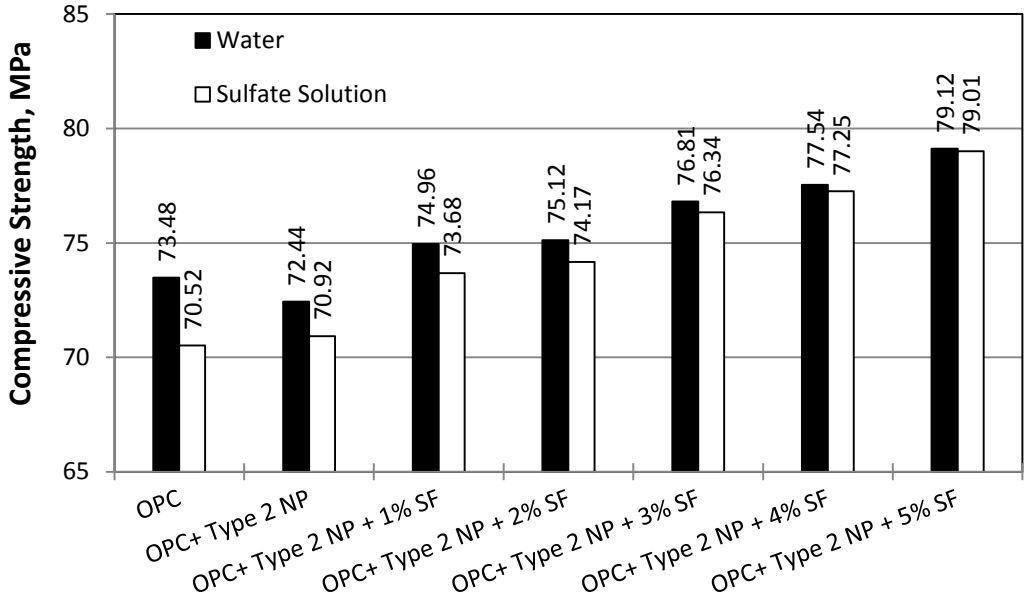

Figure 4-94: Compressive strength of OPC and Type 2 NP with varying SF placed in water and sulfate solution for 12 months

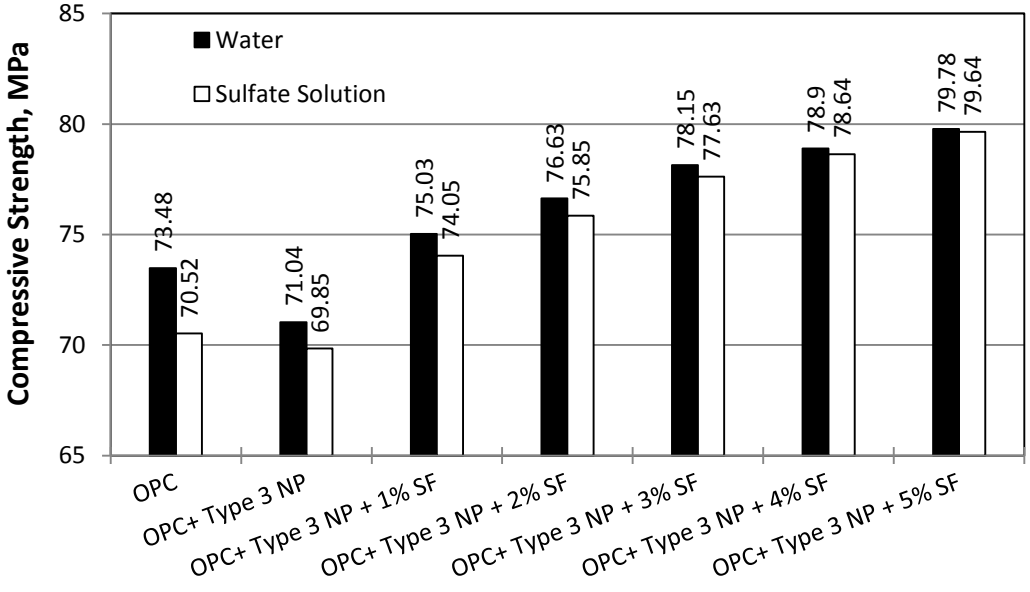

Figure 4-95: Compressive strength of OPC and Type 3 NP with varying SF placed in water and sulfate solution for 12 months

4.7.4 Effect of Chemical Activation of Natural Pozzolan by Sulfate Attack

Addition of HL did not work well for any of the three types of NP to improve the sulfate resistance of concrete. In fact, the specimens prepared with the addition of HL exhibited the highest surface deterioration among all the specimens in this study. Figures 4-96, 4-97 and 4-98 show the graphical representation of these results. The loss of compressive strength of NP specimens after 12 months of exposure to sulfate environment, increased with the addition of HL. For Type 2 and 3 NPs, the strength loss is comparable to that of OPC. Table 4-35, 4-36 and 4-37 show the strength loss of specimens prepared with 7% HL and 20% Type 1, 2 and 3 NPs, respectively. After 12 months of exposure to sulfate solution, the compressive strength loss for specimens prepared with HL was in a range of 2.91 to 4.11% while it was 4.03% in OPC specimens.. In Section 4.1.3, Figures 4-8 to 4-10 present the compressive strength development of the specimens prepared with HL. It is noted that the specimens prepared with HL showed lower compressive strength than that of OPC after 28 days of water curing. However, after 180 days of water curing the strength of specimens prepared with HL was higher than that of OPC. This may reflect that the reaction between HL and NP was not completed after 28 days of water curing and still some amount of Lime was present in the specimens. This presence of lime increased the alkalinity of the concrete which resulted in accelerated sulfate attack, when exposed to sulfate solution (acidic) after 28 days of water curing.

Table 4-35: Compressive strength loss of OPC and Type 1 NP plus HL

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Sulfate Solution	
100% OPC	73.48	70.52	4.03%
80% OPC + 20% Type 1 NP	71.86	70.61	1.74%
73% OPC + 20% Type 1 NP + 7% HL	77.30	75.05	2.91%

Table 4-36: Compressive strength loss of OPC and Type 2 NP plus HL

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Sulfate Solution	
100% OPC	73.48	70.52	4.03%
80% OPC + 20% Type 2 NP	72.44	70.92	2.10%
73% OPC + 20% Type 2 NP + 7% HL	78.09	74.88	4.11%

Table 4-37: Compressive strength loss of OPC and Type 3 NP plus HL

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Sulfate Solution	
100% OPC	73.48	70.52	4.03%
80% OPC + 20% Type 3 NP	71.04	69.85	1.68%
73% OPC + 20% Type 3 NP + 7% HL	78.93	75.96	3.76%

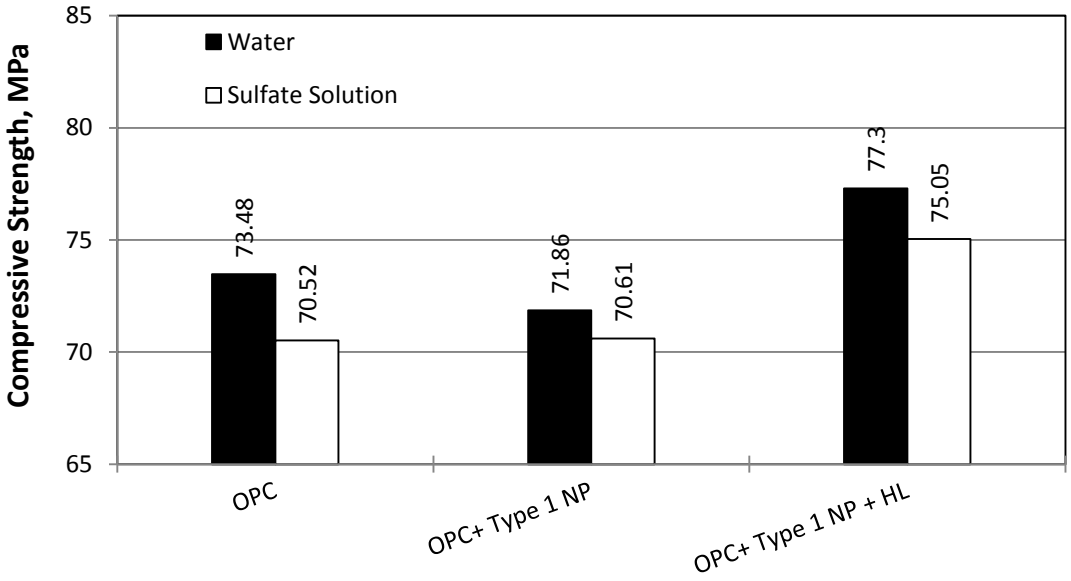

Figure 4-96: Compressive strength of OPC and Type 1 NP plus HL placed in water and sulfate solution after 12 months of exposure

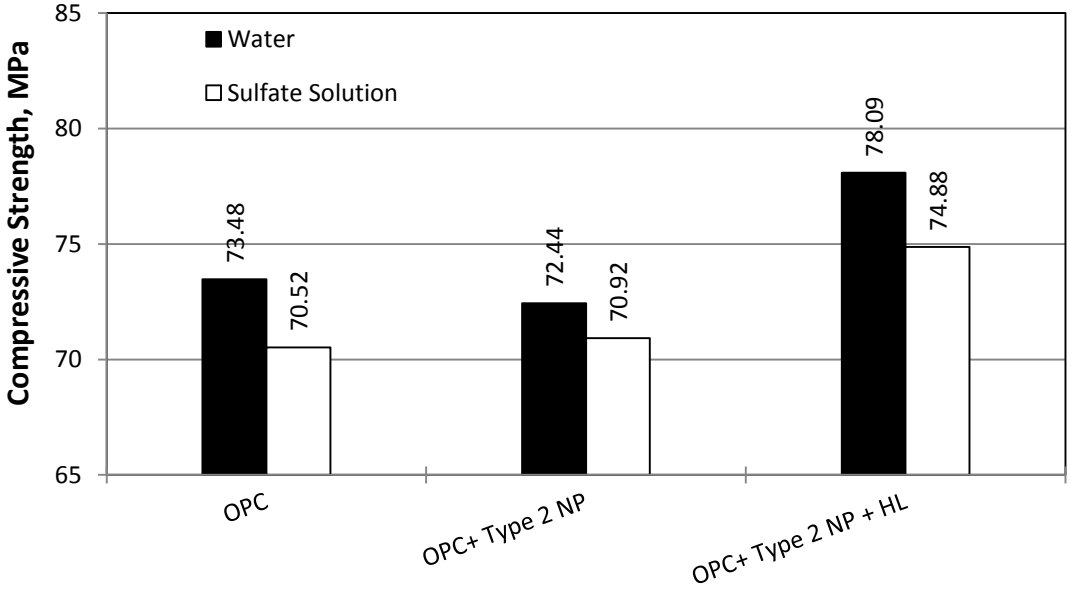

Figure 4-97: Compressive strength of OPC and Type 2 NP plus HL placed in water and sulfate solution after 12 months of exposure

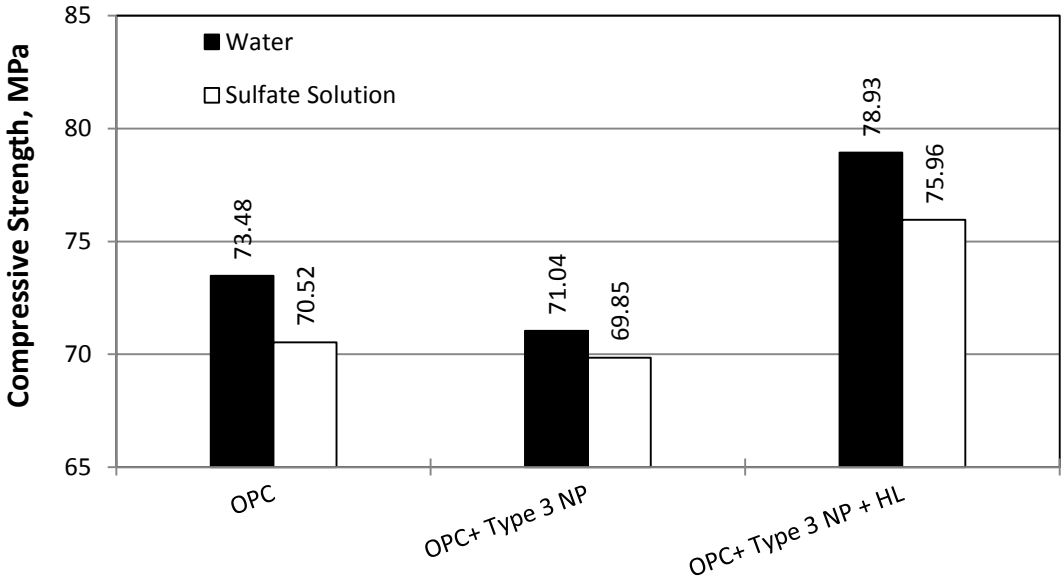

Figure 4-98: Compressive strength of OPC and Type 3 NP plus HL placed in water and sulfate solution 12 months of exposure

4.7.5 Effect of Mechanical Activation of Natural Pozzolan on Sulfate Attack

Tables 4-38, 4-39 and 4-40 summarize the strength loss in specimens prepared using finer NP. Figures 4-99, 4-100 and 4-101 show the graphical representation of the data in these tables. It can be noted that increasing the fineness of NP helped in decreasing the strength loss due to sulfate attack. After 12 months of exposure to sulfate environment, the specimens with finer NP showed less strength loss than that of coarser NP. After 12 months of exposure to sulfate environment the strength loss in finer NPs was in a range of 0.84 to 1.21% compared to 1.68 to 2.1% in coarser NPs. This improvement was not significant.

Table 4-38: Compressive strength loss in finer Type 1 NP

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Sulfate Solution	
100% OPC	73.48	70.52	4.03%
80% OPC + 20% Type 1 NP	71.86	70.61	1.74%
80% OPC + 20% Type 1 NP (Fine)	74.78	74.03	1.00%

Table 4-39: Compressive strength loss in finer Type 2 NP

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Sulfate Solution	
100% OPC	73.48	70.52	4.03%
80% OPC + 20% Type 2 NP	72.44	70.92	2.10%
80% OPC + 20% Type 2 NP (Fine)	75.12	74.21	1.21%

Table 4-40: Compressive strength loss in finer Type 3 NP

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Sulfate Solution	
100% OPC	73.48	70.52	4.03%
80% OPC + 20% Type 3 NP	71.04	69.85	1.68%
80% OPC + 20% Type 3 NP (Fine)	75.00	74.37	0.84%

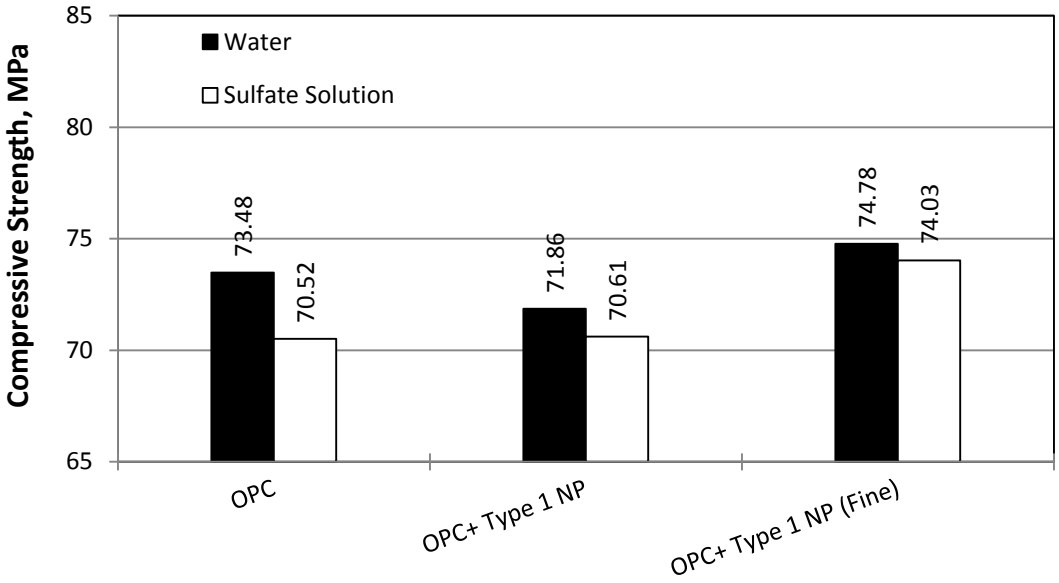

Figure 4-99: Compressive strength of coarse and fine Type 1 NP after 12 months exposure to sulfate solution

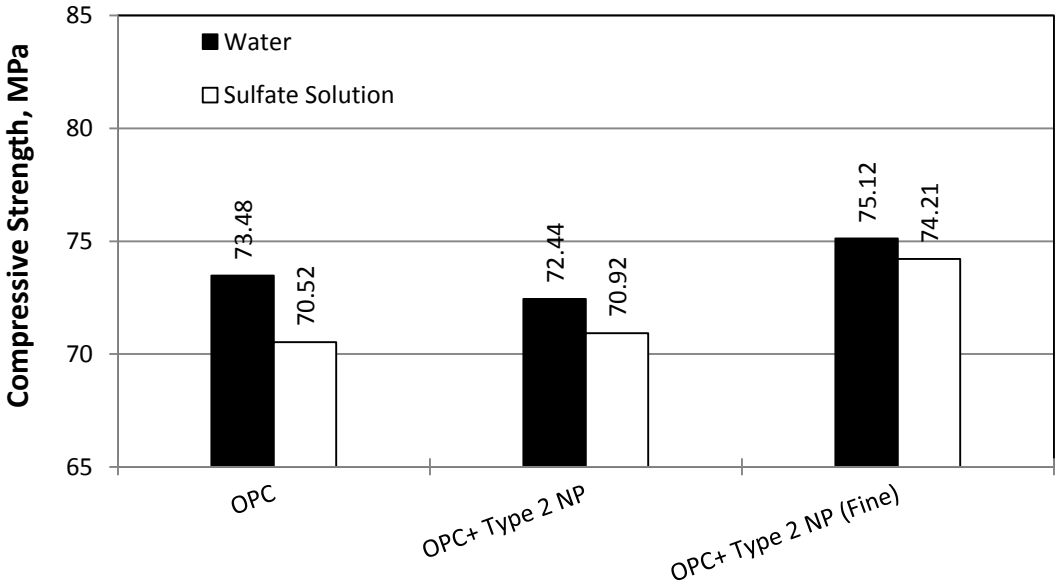

Figure 4-100: Compressive strength of coarse and fine Type 2 NP after 12 months exposure to sulfate solution

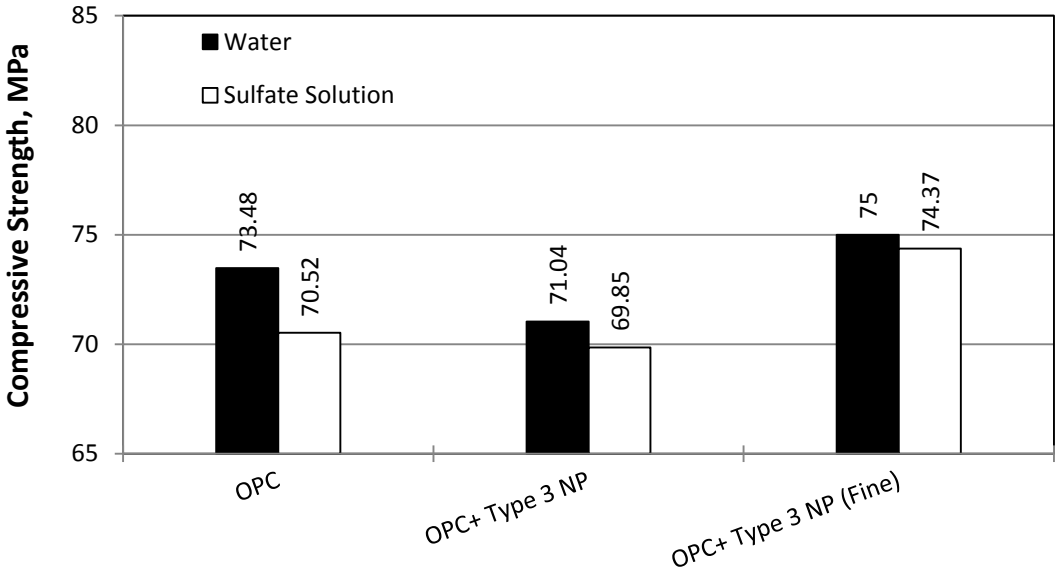

Figure 4-101: Compressive strength loss of coarse and fine Type 3 NP after 12 months of exposure to sulfate solution

4.7.6 Sulfate Attack on NP-Blended Cements

Figure 4-102 indicates that replacing OPC by NP-blended cements to prepare concrete specimens decreased the loss of strength due to sulfate attack. After 12 months of exposure to sulfate solution, the specimens prepared with NP-blended cements exhibited less strength loss than that of OPC. The loss of strength in both the blended cements was about 1% compared to 4.03% in OPC. Also, these specimens showed less strength loss compared with the specimens prepared with the replacement of 20% OPC by NPs, which was in a range of 1.7% to 2.1%. The specimens, when prepared with blended cements, are expected to have less permeability than that of OPC which than reflects in high durability performance. Table 4-41 shows the strength loss in compressive strength of NP-blended cement concrete specimens.

Table 4-41: Compressive strength loss of OPC and NP-blended cement concrete

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Sulfate Solution	
100% OPC	73.48	70.52	4.03%
NP-blended Cement 1	75.81	75.02	1.04%
NP-blended Cement 2	76.56	75.85	0.93%

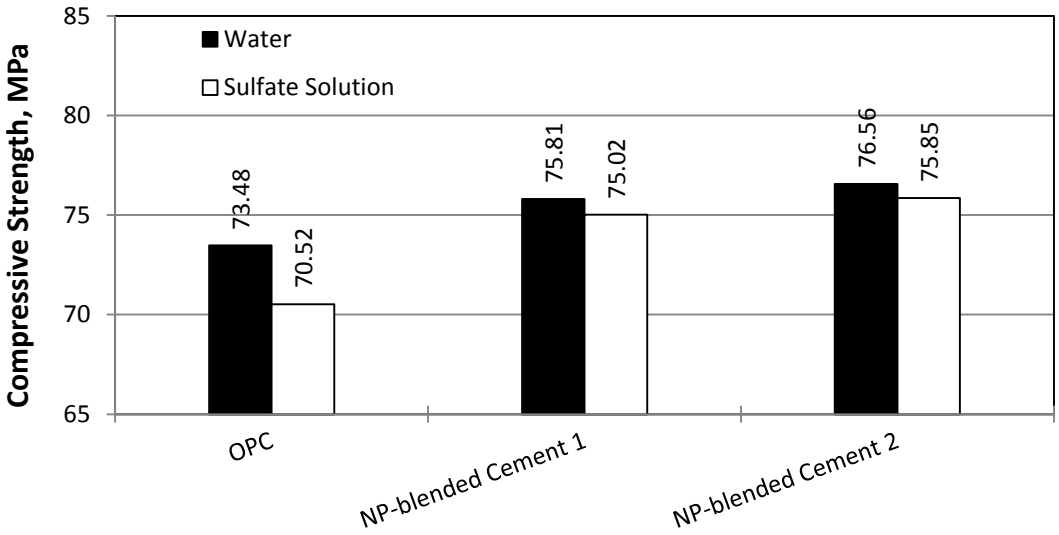

Figure 4-102: Compressive strength of OPC and NP-blended cement concretes after 12 months of exposure to sulfate solution

4.8 Salt Weathering

Concrete specimens prepared in this study were exposed to a salty solution with sabkha concentration to investigate the effects of salt weathering. The specimens were subjected to wet and dry cycles. After six and 12 months of exposure, the specimens were visually

examined for any signs of surface deterioration and then the compressive strength was measured to determine the strength loss after the exposure period.

There are two aspects to this test. First, sabkha salt concentration is used, which is rich in chloride salts with some percentage of sulfate salts. There is very little or no chemical deterioration of concrete associated with chloride salts. It is mainly the reinforcement embedded inside this concrete which is affected by chlorides. This means that the only deterioration that we are looking for is the surface erosion of concrete specimens due to the accumulation of salts when they are wet, and the volume increase of those salt crystals when they are dry. This is purely physical deterioration that is known as salt crystallization, which is caused by wet/dry cycles with water containing crystalline salts like NaCl [46, 73].

Second is the loss of strength due to wet and dry cycles. Since the strength of these specimens, which are subjected to wet/dry cycles, is to be compared with the strength of specimens of the same age which were continuously kept submerged under water; it was expected that the strength of samples subjected to wet/dry cycles would be less. Surface deterioration is discussed under visual examination in Section 4.8.1, as this deterioration is inspected visually. However, the loss of strength is discussed individually, for each type of concrete.

4.8.1 Visual Examination

Figures 4-103 through 4-111 show the concrete specimens after 6 and 12 months of exposure. Figure 4-103 shows OPC specimens and it may be noted that there was almost no surface deterioration observed on these specimens even after 12 months of exposure. Figure 4-104 shows the top of OPC specimen. This figure has its own significance, as it is the horizontal surface which is expected to have more deterioration than the circumferential surface as the amount of salt accumulated on horizontal surface is more than that on circumferential surface. This figure also suggests that there is no deterioration in OPC specimens.

Figure 4-105 shows the specimens prepared with Type 1 NP as a 20% replacement of OPC. These specimens did not show any sign of surface deterioration after 6 months but after 12 months of exposure, the specimens started to show some signs of surface deterioration. Figure 4-106 shows the top surface of specimens prepared with 20% Type 1 NP. It was seen that this horizontal surface had more deterioration as compared to vertical surface.

Figures 4-107 and 4-108 depict the specimens containing SF. These specimens too, showed surface deterioration after 12 months of exposure. Figure 4-109 shows the specimens prepared with HL and it could be noted that even after 12 months of exposure, the specimens did not show any signs of deterioration. Figure 4-110 show the specimens prepared with fine NP. These samples showed some signs of deterioration after 12 months of exposure.

As discussed in Sections 4.2 and 4.4 the addition of pozzolanic materials like natural pozzolan and silica fume reduce the permeability of concrete. Also, the addition of these materials reduces the average diameter of pores, compared to OPC concrete. [73]. Since the pores in concrete prepared with blended cements have smaller diameter than that of OPC, the salt present in these pores, when dry and increase its volume, exerts more pressure on the walls of the pores. This result in more surface deterioration of concrete prepared with blended cements than that with OPC.

As discussed in Section 4.2.3, Zelic et al. [29] studied the ternary mixes of OPC-lime-SF and reported that adding lime to OPC-SF increased the porosity of mortars. This increase in the porosity may be the reason that the deterioration of specimens prepared with HL was less than that of any other specimens prepared with pozzolanic materials.

Figure 4-103: OPC specimens after 6 (Left) and 12 months (Right) of exposure to salt solution

Figure 4-104: OPC specimen (Top surface) after 12 months of exposure to salt solution

Figure 4-105: NP specimens after 6 (Left) and 12 months (Right) of exposure to salt solution

Figure 4-106: NP specimen (Top surface) after 12 months of exposure to salt solution

Figure 4-107: NP specimens with 1% SF after 6 (Left) and 12 months (Right) of exposure to salt solution

Figure 4-108: NP specimens with 5% SF after 12 months of exposure to salt solution

Figure 4-109: NP specimens with HL after 6 (Left) and 12 months (Right) of exposure to salt solution

Figure 4-110: Specimens of fine NP after 6 (Left) and 12 months (Right) of exposure to salt solution

4.8.2 Effect of Natural Pozzolan Addition as a Partial Replacement of OPC on Salt Weathering

Table 4-42 summarizes the percentage strength loss of OPC and 20% NP (All three types). This strength loss is for the specimens which were subjected to wet/dry cycles in salt solution for 12 months. Their strength was compared with their counterpart specimens which were kept submerged under water for same period of time. It was observed that the specimens with 20% NP exhibited less strength loss than OPC specimens. After 12 month of wet/dry cycles with salt solution the strength loss in concrete specimens of all three types of NP was around 6% compared to 9% in OPC specimens. This indicates that the partial replacement of OPC with NP increased the resistance of concrete to wet/dry cycles. Addition of natural pozzolan in mixture reduces the bleeding and helps in moisture retention. [63,66]. This retention of moisture and less bleeding keeps the core concrete moist even if it is subjected to wet/dry cycles. This

means that, when subjected to wet/dry cycles, more volume of the core concrete remains moist and keeps on hydrating in NP concrete specimens than that in OPC, resulting in less strength loss of NP concrete specimens than that of OPC.

Table 4-42: Compressive strength of OPC and NP after 12 months of exposure to salt solution

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Salt Solution Wet/Dry cycle	
100% OPC	73.48	66.79	9.11%
80% OPC + 20% Type 1 NP	71.86	67.60	5.93%
80% OPC + 20% Type 2 NP	72.44	68.04	6.07%
80% OPC + 20% Type 3 NP	71.04	67.00	5.68%

4.8.3 Effect of Physical Activation of Natural Pozzolan on Salt Weathering

Tables 4-43 through 4-45 summarize the compressive strength of specimens prepared with 20% NPs and varying content of SF subjected to 12 months of wet/dry cycles in salt solution. The addition of SF to all three types of NP had clearly improved the resistance to damage due to wet/dry cycles. The loss of compressive strength in OPC was 9.11% while it was noted to be in a range between 2.21 to 2.89% when 1 to 5% SF was added to all three types of NPs. Therefore, varying the SF content did not show any appreciate effect on the resistance of concrete to retain its compressive strength due to wet/dry cycles in salt solution.

Table 4-43: Compressive strength of OPC and Type 1 NP with SF after 12 months of exposure to salt solution

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Salt Solution Wet/Dry Cycle	
100% OPC	73.48	66.79	9.11%
80% OPC + 20% Type 1 NP	71.86	67.60	5.93%
79% OPC + 20% Type 1 NP + 1% SF	74.12	72.97	2.21%
78% OPC + 20% Type 1 NP + 2% SF	74.83	73.98	2.62%
77% OPC + 20% Type 1 NP + 3% SF	76.06	75.55	2.43%
76% OPC + 20% Type 1 NP + 4% SF	77.31	76.96	2.24%
75% OPC + 20% Type 1 NP + 5% SF	78.21	78.06	2.37%

Table 4-44: Compressive strength of OPC and Type 2 NP with SF after 12 months of exposure to salt solution

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Salt Solution Wet/Dry Cycle	
100% OPC	73.48	66.79	9.11%
80% OPC + 20% Type 2 NP	72.44	68.04	6.07%
79% OPC + 20% Type 2 NP + 1% SF	74.96	72.48	2.31%
78% OPC + 20% Type 2 NP + 2% SF	75.12	72.87	2.23%
77% OPC + 20% Type 2 NP + 3% SF	76.81	74.21	2.52%
76% OPC + 20% Type 2 NP + 4% SF	77.54	75.58	2.38%
75% OPC + 20% Type 2 NP + 5% SF	79.12	76.36	2.42%

Table 4-45: Compressive strength of OPC and Type 3 NP with SF after 12 months of exposure to salt solution

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Salt Solution Wet/Dry Cycle	
100% OPC	73.48	66.79	9.11%
80% OPC + 20% Type 3 NP	71.04	67.00	5.68%
79% OPC + 20% Type 3 NP + 1% SF	75.03	73.09	2.59%
78% OPC + 20% Type 3 NP + 2% SF	76.63	74.57	2.69%
77% OPC + 20% Type 3 NP + 3% SF	78.15	76.02	2.73%
76% OPC + 20% Type 3 NP + 4% SF	78.90	76.68	2.82%
75% OPC + 20% Type 3 NP + 5% SF	79.78	77.95	2.29%

4.8.4 Effect of Chemical Activation of Natural Pozzolan on Salt Weathering

Tables 4-46 through 4-48 show the compressive strengths of specimens prepared with 20% NPs and HL and subjected to 12 months of wet/dry cycles in salt solution. For all the three Types of NP as shown in Tables 4-46 to 4-48, the addition of HL has clearly improved the resistance of concrete against the strength loss due to wet/dry cycles in salt solution. The loss of strength was 9.11% in OPC while it was noted to be around 4% for the specimens prepared with HL.

Table 4-46: Compressive strength of OPC and Type 1 NP with HL after 12 months of exposure to salt solution

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Salt Solution Wet/Dry Cycle	
100% OPC	73.48	66.79	9.11%
80% OPC + 20% Type 1 NP	71.86	67.60	5.93%
73% OPC + 20% Type 1 NP + 7% HL	77.30	74.35	3.81%

Table 4-47: Compressive strength of OPC and Type 2 NP with HL after 12 months of exposure to salt solution

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Salt Solution Wet/Dry Cycle	
100% OPC	73.48	66.79	9.11%
80% OPC + 20% Type 2 NP	72.44	68.04	6.07%
73% OPC + 20% Type 2 NP + 7% HL	78.09	74.71	4.33%

Table 4-48: Compressive strength of OPC and Type 3 NP with HL after 12 months of exposure to salt solution

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Salt Solution Wet/Dry Cycle	
100% OPC	73.48	66.79	9.11%
80% OPC + 20% Type 3 NP	71.04	67.00	5.68%
73% OPC + 20% Type 3 NP + 7% HL	78.93	76.00	3.71%

4.8.5 Effect of Mechanical Activation of Natural Pozzolan on Salt Weathering

Increasing the fineness of NP worked for all three types of NP. The reduction in compressive strength of finer NP concrete due to wet/dry cycles in salt solution was less than that of coarser NP. The reduction in strength for OPC was 9.11% while it was around 6% in coarser NP concrete specimens. The reduction in finer NP concrete specimens was around 3% which is less than that of OPC and coarser NP concrete specimens. Tables 4-49 through 4-51 show the compressive strength of finer NP concrete specimens, after 12 months of exposure to salt solution.

Table 4-49: Compressive strength of OPC and finer Type 1 NP after 12 months of exposure to salt solution

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Salt Solution Wet/Dry Cycle	
100% OPC	73.48	66.79	9.11%
80% OPC + 20% Type 1 NP	71.86	67.60	5.93%
80% OPC + 20% Type 1 NP (Fine)	74.78	72.42	3.15%

Table 4-50: Compressive strength of OPC and finer Type 2 NP after 12 months of exposure to salt solution

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Salt Solution Wet/Dry Cycle	
100% OPC	73.48	66.79	9.11%
80% OPC + 20% Type 2 NP	72.44	68.04	6.07%
80% OPC + 20% Type 2 NP (Fine)	75.12	73.14	2.64%

Table 4-51: Compressive strength of OPC and finer Type 3 NP after 12 months of exposure to salt solution

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Salt Solution Wet/Dry Cycle	
100% OPC	73.48	66.79	9.11%
80% OPC + 20% Type 3 NP	71.04	67.00	5.68%
80% OPC + 20% Type 3 NP (Fine)	75.00	72.86	2.85%

4.8.6 Resistance of NP-Blended cements Concrete to Salt Weathering

Table 4-52 summarizes the compressive strength of specimens prepared with both NP-blended cements and subjected to wet/dry cycles for 12 months. The usage of NP-blended cements in place of OPC has decreased the strength loss due to exposure to wet/dry cycles in salt solution. The strength loss for both the NP-blended cement concrete was 3.43% and 4.10% compared to 9.11% in OPC concrete.

Table 4-52: Compressive strength of OPC and NP-blended cements after 12 months of exposure to salt solution

Cementitious Materials	Compressive Strength, MPa		Loss in Strength, %
	Water	Salt Solution Wet/Dry Cycle	
100% OPC	73.48	66.79	9.11%
NP-blended Cement 1	75.81	73.21	3.43%
NP-blended Cement 2	76.56	73.42	4.10%

4.9 Carbonation

50 mm cubic specimens of mortar were prepared, submerged in water to cure for 28 days and then they were exposed to accelerated carbonation environment (3% by volume), to study the resistance of blended cements to carbonation. It has been known that with the addition of pozzolanic material in pastes, mortars and concretes, as a partial replacement of OPC, the resistance to carbonation decreases [41-45]. It is reported that up on good curing (28 days water curing), the blended cements exhibit no or very marginal increase in depth of carbonation compared to that of OPC [42] but, it is also been reported that even after one year of curing; submerged under water blended cements with fly ash and silica fume showed higher depths of carbonation than that of OPC [45]. Kritsada and Lutz [41] and Jones [43] cured the specimens for 28 days while Borge [44] cured the specimens for 90 days. All of them reported that as the blending material content increased in the cement, there was an increase in the depth of carbonation. With less curing of blended cements, the hydration of blended cements is not completed which

makes the micro-structure porous and ingress of carbon dioxide progresses to greater depths than that of OPC [46]. While with more curing, the hydration of blended cements is completed, almost all of the calcium hydroxide is consumed by pozzolanic reaction, leaving behind very little amount which calcinates quickly. With this less amount of calcium hydroxide, there is almost no buffer for C-S-H and it starts to calcinate and thus the carbonation depth is still more than that of OPC [44].

4.9.1 Effect of Natural Pozzolan Addition as a Partial Replacement of OPC on Carbonation

Table 4-52 summarizes the depths of carbonation in specimens after 90 and 180 days of exposure to accelerated carbonation environment. The depth of carbonation had clearly increased with the addition of NP to OPC. After 180 days of exposure, Type 2 NP mortar showed the highest depth; 17 mm, which is clearly very high against the depth of 11.3 mm of OPC specimen. This increment is about 50%. Types 1 and 3 NPs have a carbonation depth of 15 and 14.3 respectively, which accounts for an increase of 32.7 and 26.5% in carbonation depth compared to that of OPC. Also, it was observed that the depth of carbonation had increased for all three types of NP and OPC with time. Addition of pozzolanic material like natural pozzolan consumes the lime in the concrete and reduces the alkalinity. This drop in pH results in higher carbonation depths observed in blended cement concretes [63].

Table 4-53: Depth of Carbonation of OPC and NPs

Cementitious Materials	Carbonation Depth, mm		% Increase at 180 Days
	90 Days	180 Days	
100% OPC	8.0	11.3	-
80% OPC + 20% Type 1 NP	10.7	15.0	32.7
80% OPC + 20% Type 2 NP	12.0	17.0	50.4
80% OPC + 20% Type 3 NP	11.7	14.3	26.6

4.9.2 Effect of Physical Activation of Natural Pozzolan on Carbonation

Tables 4-53 through 4-55 summarize the depths of carbonation of mixes with varying content of SF added to all three types of NPs. With the addition of silica fume in varying dosages (1 to 5%) to NP-OPC mix, the depth of carbonation increased. By increasing the dosages of silica fume, an increase in the depth of carbonation was observed. With the addition of 1% SF the depth of carbonation in the specimens of all the three types of NPs was noted to be 15 to 17 mm compared to 11.3 mm in OPC, which is an increase of 32.7 to 50.4%. With the addition of 5% SF the depth of carbonation in the specimens of all the tree types of NPs was noted to be 20.3 to 22.0 mm which is about 79.6 to 94.6% higher than that of OPC. Similar observations have been reported in the [42, 43, 45]. As discussed in Section 4.9.1 addition of pozzolanic material increases the depth of carbonation.

Table 4-54: Depth of carbonation in Type 1 NP plus SF

Cementitious Materials	Carbonation Depth, mm		% Increase at 180 Days
	90 Days	180 Days	
100% OPC	8.0	11.3	-
80% OPC + 20% Type 1 NP	10.7	15.0	32.7
79% OPC + 20% Type 1 NP + 1% SF	11.0	15.7	38.9
78% OPC + 20% Type 1 NP + 2% SF	12.0	16.0	41.6
77% OPC + 20% Type 1 NP + 3% SF	12.0	17.0	50.4
76% OPC + 20% Type 1 NP + 4% SF	14.3	20.0	77.0
75% OPC + 20% Type 1 NP + 5% SF	14.7	20.3	79.6

Table 4-55: Depth of carbonation in Type 2 NP plus SF

Cementitious Materials	Carbonation Depth, mm		% Increase at 180 Days
	90 Days	180 Days	
100% OPC	8.0	11.3	-
80% OPC + 20% Type 2 NP	12.0	17.0	50.4
79% OPC + 20% Type 2 NP + 1% SF	12.7	16.0	41.6
78% OPC + 20% Type 2 NP + 2% SF	13.0	17.0	50.4
77% OPC + 20% Type 2 NP + 3% SF	14.3	19.7	74.3
76% OPC + 20% Type 2 NP + 4% SF	15.0	21.3	88.5
75% OPC + 20% Type 2 NP + 5% SF	16.0	22.0	94.7

Table 4-56: Depth of carbonation in Type 3 NP plus SF

Cementitious Material	Carbonation Depth, mm		% Increase at 180 Days
	90 Days	180 Days	
100% OPC	8.0	11.3	-
80% OPC + 20% Type 3 NP	11.7	14.3	26.6
79% OPC + 20% Type 3 NP + 1% SF	12.0	17.0	50.4
78% OPC + 20% Type 3 NP + 2% SF	12.3	18.0	59.3
77% OPC + 20% Type 3 NP + 3% SF	13.0	18.7	65.5
76% OPC + 20% Type 3 NP + 4% SF	14.3	20.3	79.7
75% OPC + 20% Type 3 NP + 5% SF	15.3	21.7	92.0

4.9.3 Effect of Chemical Activation of Natural Pozzolan on Carbonation

Table 4-56 through 4-58 summarize the depths of carbonation of specimens with HL and all three types of NPs. With the introduction of hydrated lime in the mix, it was observed that the depth of carbonation clearly decreased as compared with the depth of NP-OPC without HL. Still, the depths for all three types of NP are higher than that of OPC. Papadakis [45] reported that the mixes with high calcium fly ash performed better than low calcium fly ash and silica fume when subjected to carbonation. This may be because of the high volume of lime introduced in the mix which increases the alkalinity there by increasing the pH of the mix and reduce the depth of carbonation. However, the depth of carbonation in NP with HL was slightly more than that in OPC. Since the pozzolanic materials tend to increase the depth of carbonation and HL tends to reduce it, it was expected that the depth of carbonation would be higher than that of OPC and less than that of NP cement mortars.

Table 4-57: Depth of carbonation in Type 1 NP with HL

Cementitious Material	Carbonation Depth, mm		% Increase at 180 Days
	90 Days	180 Days	
100% OPC	8.0	11.3	-
80% OPC + 20% Type 1 NP	10.7	15.0	32.7
73% OPC + 20% Type 1 NP + 7% HL	9.0	13.0	15.0

Table 4-58: Depth of carbonation in Type 2 NP with HL

Cementing Blend	Carbonation Depth, mm		% Increase at 180 Days
	90 Days	180 Days	
100% OPC	8.0	11.3	-
80% OPC + 20% Type 2 NP	12.0	17.0	50.4
73% OPC + 20% Type 2 NP + 7% HL	10.0	14.3	26.6

Table 4-59: Depth of carbonation in Type 3 NP with HL

Cementing Blend	Carbonation Depth, mm		% Increase at 180 Days
	90 Days	180 Days	
100% OPC	8.0	11.3	-
80% OPC + 20% Type 3 NP	11.7	14.3	26.6
73% OPC + 20% Type 3 NP + 7% HL	9.0	12.7	12.4

4.9.4 Effect of Mechanical Activation of Natural Pozzolan on Carbonation

Tables 4-59 through 4-61 summarize the depth of carbonation for specimens prepared with both finenesses of NP used in this study. Increasing the fineness of NP did not show any profound impact on the depth of carbonation of NP despite the usage of three different pozzolans. Although there was a slight increase in the depth of carbonation but it is not very significant. The depth of carbonation in the coarser NPs was in a range of 14.3 to 17.0 mm compared to 15.0 to 17.3 mm in finer NPs specimens.

Table 4-60: Depth of carbonation in fine Type 1 NP

Cementitious Material	Carbonation Depth, mm		% Increase at 180 Days
	90 Days	180 Days	
100% OPC	8.0	11.3	-
80% OPC + 20% Type 1 NP	10.7	15.0	32.7
80% OPC + 20% Type 1 NP (Fine)	11.0	15.7	38.9

Table 4-61: Depth of carbonation in fine Type 2 NP

Cementitious Material	Carbonation Depth, mm		% Increase at 180 Days
	90 Days	180 Days	
100% OPC	8.0	11.3	-
80% OPC + 20% Type 2 NP	12.0	17.0	50.4
80% OPC + 20% Type 2 NP (Fine)	11.7	17.3	53.1

Table 4-62: Depth of carbonation in fine Type 3 NP

Cementitious Material	Carbonation Depth, mm		% Increase at 180 Days
	90 Days	180 Days	
100% OPC	8.0	11.3	-
80% OPC + 20% Type 3 NP	11.7	14.3	26.6
80% OPC + 20% Type 3 NP (Fine)	12.3	15.0	32.7

4.9.5 Carbonation of NP-Blended Cements

Table 4-62 summarizes the depths of carbonation for NP-blended cements. The specimens prepared with NP-blended cements exhibited higher depth of carbonation than that of OPC. The depth of carbonation in the specimens prepared with NP-blended cements was noted to be 12.0 and 14.0 mm compared to 11.3 mm in OPC. As discussed in Section 4.9.1 addition of natural pozzolan increases the depth of carbonation.

Table 4-63: Depth of carbonation in NP-blended cements

Cementitious Material	Carbonation Depth, mm		% Increase at 180 Days
	90 Days	180 Days	
100% OPC	8.0	11.3	-
NP-blended Cement 1	10.0	14.0	23.7
NP-blended Cement 2	9.0	12.0	6.2

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study was conducted to assess the mechanical properties and durability aspects of blended cement concretes produced by replacing 20% OPC with three different locally available natural pozzolans. Also, 1-5% silica fume and 7% hydrated lime were used with natural pozzolan to increase their reactivity physically and chemically. Some mixes were also prepared with finer natural pozzolan. The following conclusions can be drawn based on the data developed in this study:

The compressive strength of mixes with natural pozzolan was less than that of OPC at early age but it was comparable to OPC at 360 days.

Increasing the fineness of natural pozzolan and adding silica fume and hydrated lime have all worked to increase the strength of natural pozzolan mixes. The least improvement was noted in the mixes with the increased fineness.

The depth of water penetration into the mix decreased with the inclusion of natural pozzolan (both fineness) as compare to neat OPC concrete mixes. The inclusion of silica fume and hydrated lime further decreased the depth of water penetration depth.

The drying shrinkage strain of natural pozzolan mixes was less than that of OPC. Mixes with 20% natural pozzolan with 5% silica fume and 20% natural pozzolan with 7% hydrated lime, exhibited similar shrinkage strain as of OPC.

The chloride diffusion in all the blended cement concretes was much less than that in OPC concrete.

The time to initiation of reinforcement corrosion in all the blended cement concretes was more than that of OPC concrete. After 300 days of exposure, corrosion initiation was not noted in the mixes with 2% or higher quantity silica fume or with 7% hydrated lime.

The corrosion current density on steel in all blended cement concretes was much less than that on steel in the OPC concrete specimens.

Blended cement concrete exhibited better resistance to sulfate attack than OPC. Less surface deterioration and strength loss were observed in blended cement concrete than that in OPC concrete, with an exception of mixes with hydrated lime. These latter mixes showed more surface deterioration and strength loss than that of OPC.

Blended cement concretes were less affected by wet/dry cycles compared with the performance of OPC concrete under similar conditions.

The depth of carbonation in all the blended cement concrete was more than that of OPC.

5.2 Recommendations

The avenues for usage of blended cements with locally available Saudi natural pozzolan are listed in Table 5-1.

Table 5-1: Avenues for the use of blended cements or with Saudi natural pozzolan

Concrete	**Applications**
NP-20%	Medium strength structural concrete with high durability
NP-20% + SF 1-3%	Medium strength structural concrete with high durability
NP-20% + SF 4-5%	High strength structural concrete with high durability
NP-20% + HL-7%	Medium-High strength structural concrete with high durability, except for structural elements subjected to high sulfate attack.

Future studies may include:

Thermal activation of natural pozzolan.

Lime-natural pozzolan system, with complete elimination of OPC.

Micro-structural studies of these blended cement concretes.

Usage of different dosages of pozzolan and HL in order to arrive at the optimum combination.

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